JOURNAL of the AIR POLLUTION CONTROL ASSOCIATION

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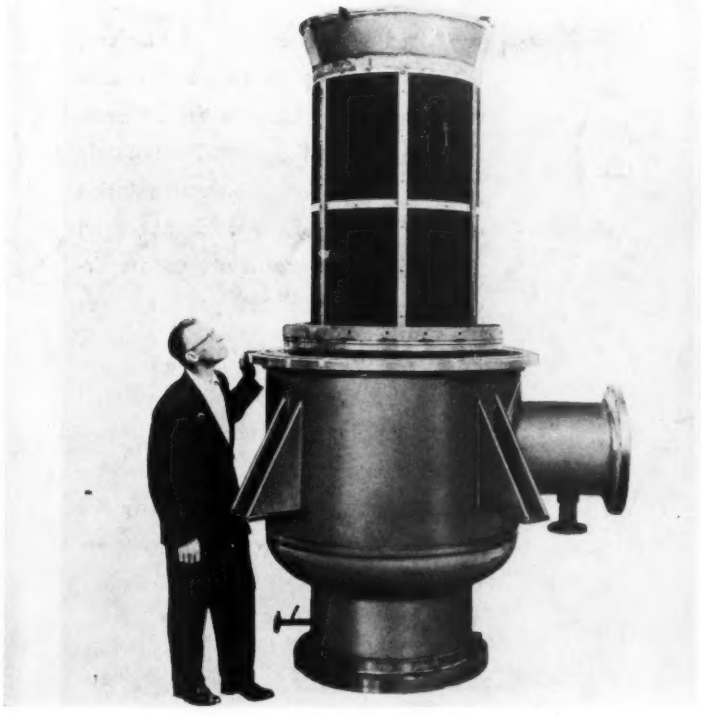
SCIENCE & TECHNOLOGY

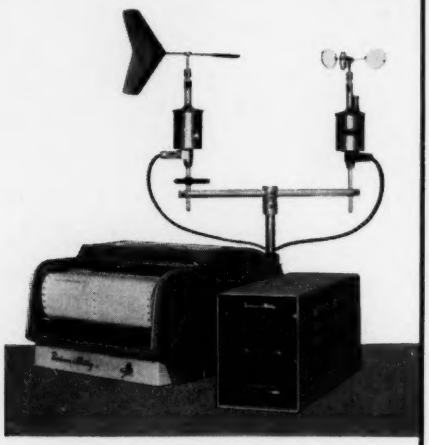


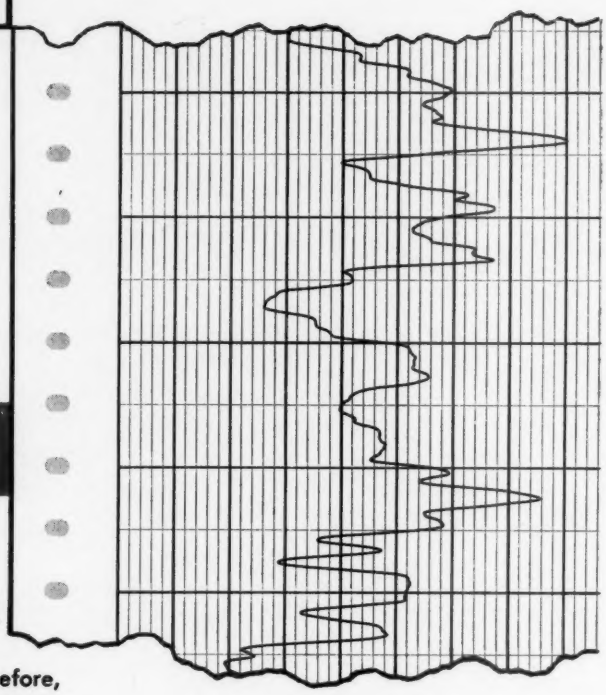
Catalytic Pressure Vessel

(See Page 212)

November 1958
Vol. 8, No. 3

WRITTEN BY THE WIND





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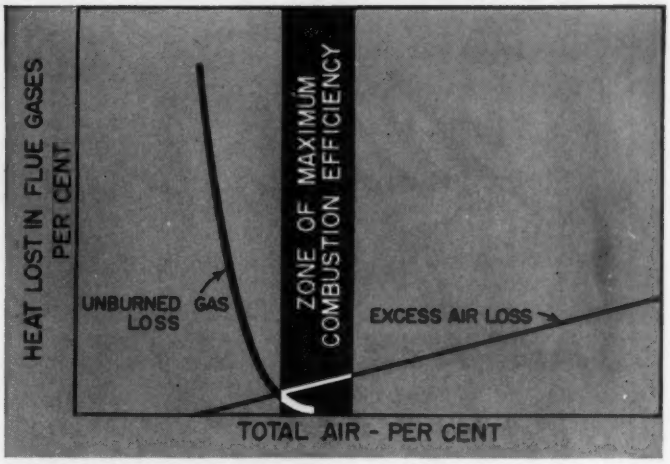
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ZONE OF MAXIMUM COMBUSTION EFFICIENCY
EXCESS AIR LOSS
TOTAL AIR - PER CENT

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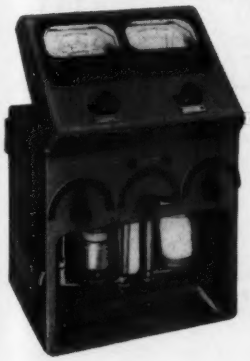

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G 40-1

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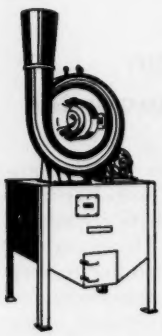
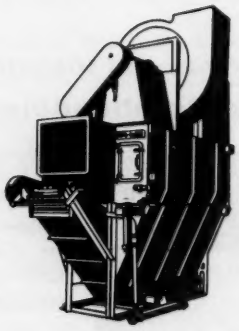


Type D ROTO-CLONE
For moderate loadings of dry, granular particles



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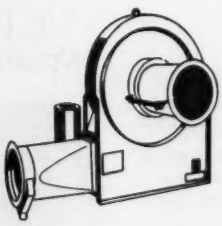

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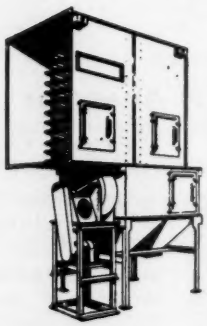

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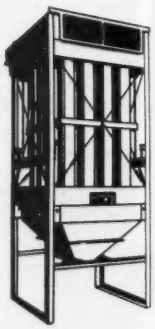

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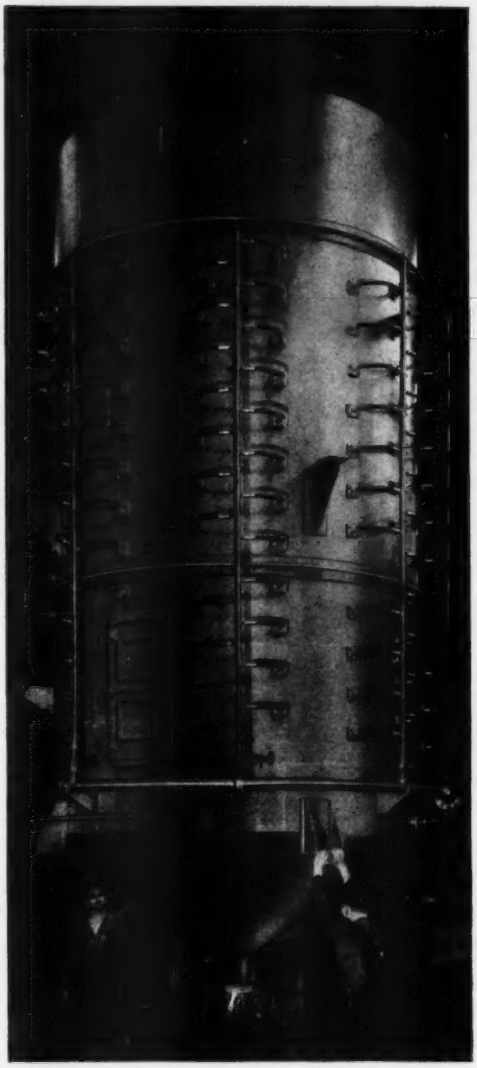

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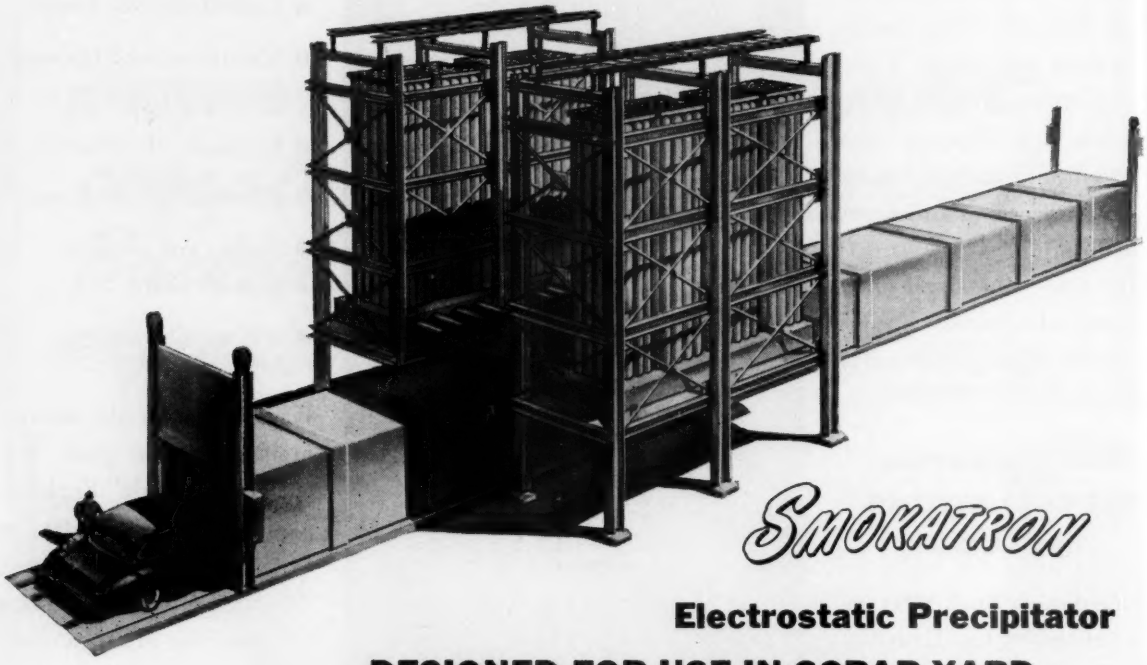

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JOURNAL OF THE AIR POLLUTION CONTROL ASSOCIATION

(Formerly "Air Repair")

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Devoted To
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The Editor welcomes writers interested in air pollution problems and encourages them to use the pages of this journal for the expression of their opinions. But neither he nor the Association assumes responsibility for the validity of the opinions expressed herein.

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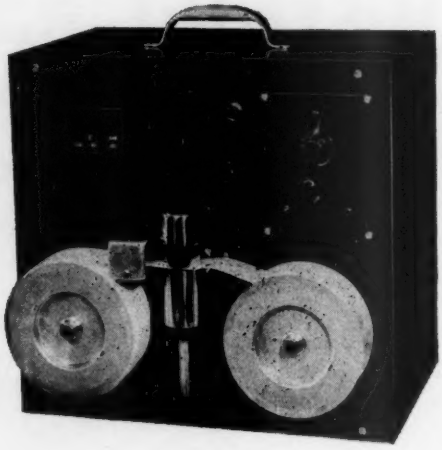
In Cincinnati, Ohio



A.I.S.I. Sampler records valuable information on finely divided soil particles in the atmosphere

Since 1952, the City of Cincinnati has been using the A.I.S.I. Sampler, and is currently using three of them in the city's continuous air measurement program.

According to Charles W. Gruber, Air Pollution Control and Heating Engineer, City of Cincinnati, the A.I.S.I. Sampler is also used as an index of soil in the atmosphere, and the results give much valuable information on the build-up and carry-away of the finely divided particles which remain suspended.

Like an increasing number of large cities throughout the country, Cincinnati is conscious of the undesirability of polluted atmosphere. Similarly, an increasing number are depending on the A.I.S.I. Sampler to record for them what contamination is in the atmosphere. They have found, too, that because of its low cost, the A.I.S.I. Sampler can be used in quantity to give complete coverage of the city. And, of course, it operates quietly and continuously 24 hours a day.

Write for further information on both the A.I.S.I. Sampler and the Hydrogen Sulfide Sampler, as well as the Spot Evaluator, which evaluates the samples by measurement of light transmission.

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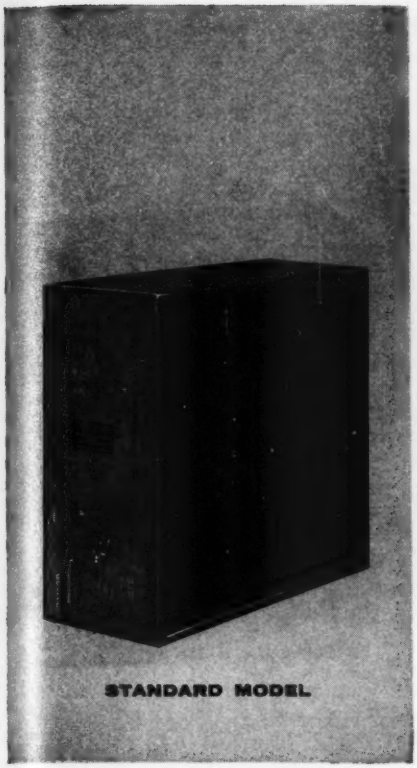
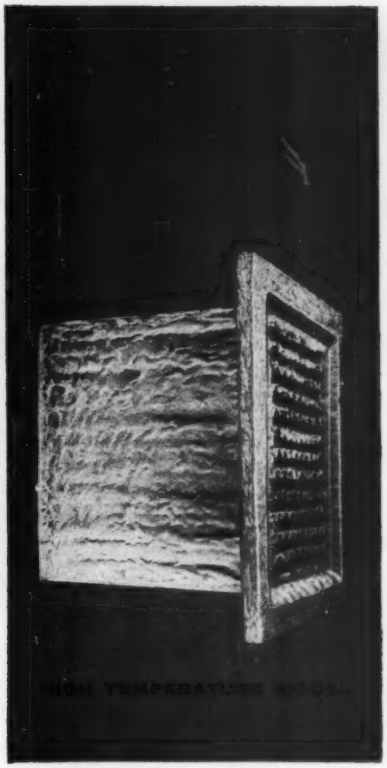


STANDARD MODEL

FIRE RESISTANT MODEL



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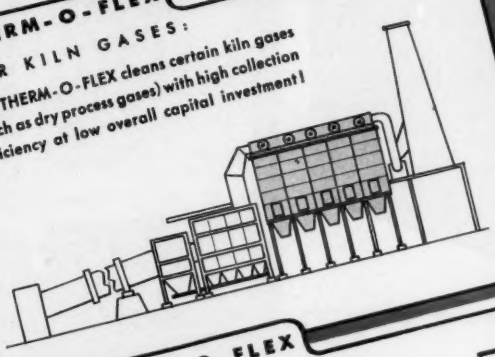

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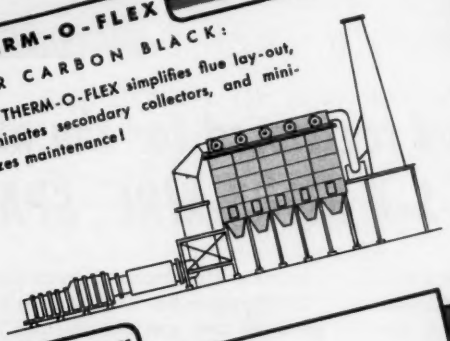

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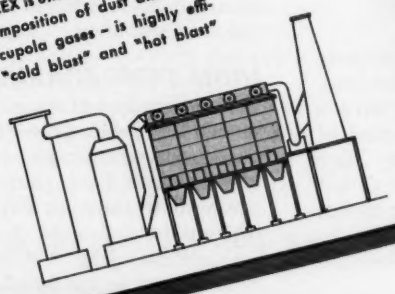

Western-Precipitation brings another important new advancement to the gas cleaning field — the THERM-O-FLEX Collector — a filter type of unit with many advantages over conventional filter equipment...

▶ The THERM-O-FLEX features glass silicone treated filter tubes that efficiently handle gases as hot as 550° F!

▶ The THERM-O-FLEX tubes are cleaned *automatically* by intermittent collapsing (not by destructive shaking). This assures uniformly low pressure drop combined with long filter life!

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THERM-O-FLEX literature will gladly be sent. Write or phone, the Western-Precipitation office nearest you.

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Simultaneous Removal of Acid Gases, Mists, and Fumes with Mineral Wool Filters*†

CHARLES E. BILLINGS, CHARLES KURKER, JR.
AND LESLIE SILVERMAN
Harvard School of Public Health
Department of Industrial Hygiene
Boston, Massachusetts

The economical control of visible effluents from open hearth furnaces and other steel producing operations is under active investigation at the Harvard Air Cleaning Laboratory through the support of the American Iron and Steel Institute. Results of laboratory [1] and field studies [2] on slag wool filters for removal of sub-micron iron oxide particles from high temperature open hearth gases have indicated that required efficiency is obtained with reasonable filter life. These filters are washed and reused. Wools can be produced from many crushed minerals [3] (blast furnace slag is typical). These are melted in furnaces with limestone usually added as a flux. The molten slag is then blown or spun into 4 to 10μ diam. fibers. A typical slag wool analysis [1] indicates approximately 40% CaO, 40% SiO_2, 10% Al_2O_3, and the remainder MgO and Fe_2O_3.

During our field studies it was observed that the wool was not as durable as in laboratory tests. Fibers used on open hearth furnace fume appeared to fracture more readily and useable life was reduced by about 20%. As a possibility it was suspected that slag wool might be reacting with acid flue gases probably from sulfur oxidation. Continuous filters in the field unit were formed from wool fibers by means of a water slurry process and were admitted to the gas stream containing from 50 to 100% residual moisture [2]. Although filters appeared to dry readily upon exposure to the high temperature gas, the presence of water and basic materials in the filter during drying could cause absorption of significant amounts of SO_2 gas with formation of sulfates from flux used during manufacture. If the flue gas contained SO_3, this could be converted to H_2SO_4 mist in saturated areas within the bed, and removed by filtration mechanisms to cause further acid attack.

Sulfur dioxide sampling during these tests [2] indicated that approximately 80 ppm. of SO_2 were present in the entering gas, and some was being removed by the filter. On the basis of this finding, laboratory tests were conducted to determine the magnitude of the removal of SO_2 and H_2SO_4 by wet and dry slag wool filters. Results were sufficiently encouraging to indicate that the method had promise for the simultaneous removal of many types of solid and liquid aerosols and acid gases in a single simple, inexpensive device.

Many commercially available slag fibers contain in excess of 25% CaO from the limestone used as a flux. Fibers offer an extended surface of basic material for diffusional transfer in acid gas absorption. A pound of 4μ slag wool fiber will have a surface area of 1800 ft.,^{2} assuming slag has a density of 172 lb./ft.^{3}. One inch thick filters packed to a density of 5 lb./ft.^{3} as used in several of these studies have a surface area of 740 ft.^{2}/square foot of filter. The laboratory test unit holds a 6 in. diam. filter, for which the fiber area is 145 ft.^{2} (1 in. thick and 5 lb./ft.^{3}). Small fiber diameter is advantageous for the collection of aerosol particles less than 0.5μ by diffusion, impaction and direct interception. In either case there is an acid-base reaction possible at the fiber surface if water is present. This can cause a leaching of the base (presumably CaO, MgO, NaO or K_2O) with formation of salts at the fiber surfaces. Material within the fiber itself is used to neutralize the acid.

Mineral wool filters have been tested for collection efficiency, resistance characteristics and useable life on a group of commonly occurring mineral acid gases and mists related to air pollution problems. Simultaneous removal of acid gas and particulate materials is a unique feature of slag wool filters which was not originally anticipated. It should be useful in air pollution applications requiring simultaneous collection of aerosol particles and acid gases. Other important aspects are that it can be used at high temperature (up to 1200°F.); and the slag wool cost is low (1 to 2c/lb.).

Fiber Characteristics

Three types of commercial mineral wool available in northeastern United States as thermal insulation were selected for study. Two slag wools were included. Bethlehem Mineral Wool

*This report is based on work performed under a contract between Harvard University and the American Iron and Steel Institute.
†Presented at the 51st Annual Meeting of the Air Pollution Control Association at Philadelphia, Pennsylvania, May 26-29, 1958.

(Mineralite) is made from blast furnace basic slag which is spun into fibers about 5.0μ in diam. and one to two in. long. Baldwin-Hill loose insulation wool is made from a mixture of copper and iron slags and has a mean fiber diameter of 4.4μ with essentially the same length. These wools will withstand temperatures up to about 1200°F., beyond which point the fibers begin to crystallize and the media becomes unuseable. Melting point of blast furnace slag is in the vicinity of 2500°F. The third mineral wool selected for tests was B & W Kawool manufactured by the Babcock and Wilcox Company. It is made by melting Kaolin clay ($Al_2O_3.2SiO_2.2H_2O$) in an electric furnace and spinning into 4μ fibers on the order of 7 to 8 in. long. Kaowool A is designated by the manufacturer as lubricated, and Kaowool B, unlubricated. We have not tested these fibers for upper temperature limit, but it should be close to 2000°F., based upon the melting point of kaolin (3200°F.).

Alkalinity was determined by placing samples of the fibers in a known amount of acid and titrating with a standard base. A summary of results is given in Table I. It can be seen that alkalinity is slightly dependent upon acid normality. Approximately (based on several tests) one gram of Mineralite fiber will react with (and neutralize) 8.5 meq. (0.31 g.) of HCl and 9.0 meq. (0.44 g.) of H_2SO_4. Baldwin-Hill fibers neutralize 6.2 meq. (0.23 g.) of HCl and 6.0 meq. (0.29 g.) of H_2SO_4.

Basic slag wool fibers neutralized about 1/3 of a gram of acid per gram of wool, Mineralite being slightly more alkaline than Baldwin-Hill. Kaowool fibers were effectively neutral to the two acids used.

Test Procedures

The three types of wool selected for study were tested dynamically for removal efficiency, filter resistance changes, and operating life on some of five gases, four mists and three solid particulate fumes. Performance was measured at various filtering velocities (ranging from 50 to 200 fpm.), both dry and wet, and at room and elevated temperatures.

Bulk fibers of Mineralite, Baldwin-Hill, and Kaowool (Types A and B) were formed into 6 in. diam. by 1 and 2 in. thick filters from a 1% water slurry. In wet filter tests, pads were allowed to drain until most of the water had run off. The majority of tests were performed with dry filters, in which case the pads were first drained as above, and then placed on a hot plate until dry.

Filters were placed in a 6 in. diam. test unit (Ref. 1, Fig. 3) and exposed to various concentrations of acid gases, mists, and fumes. Volume of air flow through the filters was measured with a calibrated sharp-edged orifice located downstream of the test pad. Gas flow resistance of filters was measured by means of wall static pressure taps (located adjacent to each face of the filter) connected to a vertical liquid manometer. High gas temperatures were measured with thermometers placed before and after the filter.

Methods of generation, sampling, and analysis of gas mixtures and aerosols varied with the nature of the test. Techniques are described briefly in each section, and are summarized in Table II (*see page 187*).

Acid Gas Removal

A. *Sulfur Dioxide (SO_2)*

Since SO_2 is probably the major sulfur contaminant present in flue gases from combustion of sulfur bearing fuels, its action on mineral wool filters was investigated first. The study was undertaken to determine the extent of fiber attrition caused by SO_2 under known conditions and to determine if effects were comparable to field studies. Effects of changes in operating variables (i.e., gas velocity, SO_2 concentration, filter moisture content) were investigated because of the potential uses of this material for the simultaneous collection of aerosol particles and gases in other air pollution control applications.

As a preliminary test, samples of Mineralite and Baldwin-Hill slag wools were exposed to static atmospheres of 500 and 5000 ppm. SO_2 in closed containers. Samples were placed in three liter flasks containing a small amount of water on the bottom, a known volume of SO_2 was admitted, and wool was exposed for a period of three days. Microscopic examination of wools upon removal indicated that Mineralite fibers had decreased in size from 5.0 to 3.0μ

TABLE I

Characteristics of Mineral Wools Used in Acid Gas, Mist and Fume Investigations

Wool Manufacturer	Acid	Normality	Alkalinity[a] meq. acid/ g. of wool	Fiber Characteristics
Bethlehem	HCl	0.1	3.6	Basic Blast Furnace
Mineral Wool	HCl	0.3	9.9	Slag (White)
(Mineralite),	HCl	1.0	12.2	5.0μ diam., 1 to
Bethlehem Steel Co.,	H_2SO_4	0.1	3.2	2 in. long
Bethlehem, Pa.	H_2SO_4	0.3	9.4	
	H_2SO_4	0.7	14.3	
Baldwin-Hill Co.				
Trenton, New Jersey	HCl	0.1	2.8	Mixed Copper and Iron
	HCl	0.3	6.0	Slag. (Gray)
	HCl	1.0	6.0	4.4μ diam., 1 to
	H_2SO_4	0.1	2.6	2 in. long
	H_2SO_4	0.3	7.0	
	H_2SO_4	0.7	8.5	Kaolin Wool (White)
B & W Kaowool	A HCl	0.1	0.2	"A" Lubr. "B" Unlubr.
Babcock & Wilcox Co.,	A HCl	0.7	0.3	4μ diam.
New York 17, New York	B H_2SO_4	0.1	0.1	7 to 8 in. long
	B H_2SO_4	0.7	0.3	

a One meq. HCl is 0.0365 g. of acid; one meq. H_2SO_4 is 0.0490 g. of acid.

TABLE II
Methods of Generation, Sampling and Analysis For Test Contaminants

Composition	Concentration	Approx. MMD μ	Generation Method	Sampling Method	Analytical Method
Gases					
SO_2	110-400 ppm.	—	Comm. Cyl. Gas	Sintered Glass Absorbers with hydrogen peroxide solution.	Electrical Conductivity
NO_2	30-35 ppm.	—	Comm. Cyl. Gas	Sintered Glass Absorbers with Sulfanilic acid and alpha-naphthylamine reagent.	Colorimetrically
HCl	55-1000 ppm.	—	Comm. Cyl. Gas	Sintered Glass Absorbers with water	Electrical Conductivity
HF	250-580 ppm.	—	Comm. Cyl. Gas	Sintered Glass Absorbers with water	Bleaching action of F^- on ferric thiocyanate
SiF_4	100-420 ppm.	—	Comm. Cyl. Gas	Millipore Filters followed by sintered glass absorbers with water	Bleaching action of F^- on ferric thiocyanate
Mists					
H_2SO_4	320-2000 mg./m.^{3}	0.7	50% solution vaporized on hot plate and recondensed in inlet air stream	Millipore Filters	Titration with NaOH
H_2SO_4	65-120 mg./m.^{3}	2.0	Atomization of conc. acid plus impingement and elutriation	Millipore Filters	Electrical Conductivity
SO_3	35-100 mg./m.^{3}	0.5	Heating fuming acid; mist separated in electrostatic precipitator	Millipore Filters followed by sintered glass absorbers with water	Electrical Conductivity
HNO_3	125-315 mg./m.^{3}	2.0	Atomization of 80% acid plus impingement and elutriation	Millipore Filters followed by sintered glass absorbers with water	Colorimetrically with Brucine reagent
H_3PO_4	45-110 mg./m.^{3}	1.5	Sublimed from solid P_2O_5 and passed vapor through water to form mist	Millipore Filters	Electrical Conductivity
Fumes					
Fe_2O_3	0.01-0.15 gr./ft.^{3}	0.5	Combustion of Iron Pentacarbonyl ($Fe(CO)_5$)	MSA-1106-B Glass Filter Paper	Gravimetrically; or Iron Analysis by alpha-alpha-dypyridyl, colorimetrically
$NH_4F.HF$	0.2 gr./ft.^{3}	0.5	Sublimation on hot plate and recondensed as solid in inlet air stream	Small Electrostatic Precipitator	Bleaching action of F^- on ferric thiocyanate
Fly Ash (A)	0.06-0.2 gr./ft.^{3}	15	Cottrell prec. fly ash resuspended with NBS Generator	Type S Pleated Filter	Gravimetrically
Fly Ash (B)	0.02-0.04 gr./ft.^{3}	8	Combustion of 40 mesh pulv. coal in flame	MSA-1106-B Glass Filter Paper	Gravimetrically

TABLE III
Slag Wool Filter Efficiency For Sulfur Dioxide Gas

Wool[a]	Filt. Vel. fpm.	Average Resistance[b] In. H_2O	Inlet SO_2 Conc. ppm.	Av. Eff. %	Operating Time Min.	Operating Temp. °F.	A.[d] %	No. of Tests	Remarks
M	50	0.6	330	0	10	80	—	1	Dry (1 in. thick)
"	"	1.1	"	0	10	300	—	1	Dry (1 in. thick)
"	"	3.7	"	21	58	80	5	1	Wet
"	"	3.0	"	30	73	170	9	2	Wet
B-H	150	2.0	210	11	10	80	0	1	Dry
"	50	4.8[c]	130	0	42	260	—	1	Dry, with iron-oxide on filter
"	150	6.6	110	24	100	80	9	3	Wet
"	150	8.7	110	29	44	400	14	1	Wet
"	150	7.8	400	21	80	80	5	1	Wet
"	50	5.0	330	21	85	80	16	2	Wet
"	50	4.7	330	7	25	160	0	1	Wet
K-A	50	4.8	330	0	10	80	—	1	Dry
"	"	6.9	"	0	12	300	—	1	Dry
"	"	9.1	"	6	24	80		1	Wet
"	"	4.8	"	49	10	120	—	1	Wet
K-B	50	3.6	330	0	10	80	—	1	Dry
"	"	5.0	"	0	10	310	—	1	Dry
"	"	12.1	"	20	37	80	—	1	Wet

a Filters tested were 2 in. thick at 4 lb./ft.^{3} packing density.
b At temperatures shown in column 7.
c Filter initially at 2.0 in. water and exposed to carbonyl-generated iron-oxide until resistance had risen to value shown, then tested on SO_2.
d Filter rating factor, pounds of SO_2 removed/100 lb. of wool, calculated from efficiency and inlet concentration.

and Baldwin-Hill fibers decreased from 4.4 to 2.6μ. Significant acid action was apparent from the decrease in median diameters. A similar decrease in fiber size was noted during exposures discussed below.

For dynamic tests, pads were placed in the 6 in. diam. test unit (dry, or with residual moisture in wet tests) and exposed to known concentrations of SO_2 in air by metering commercial cylinder gas into the open inlet of the filter test duct. Samples were collected before and after the test pad in small sintered glass absorbers containing weak sulfuric acid and hydrogen peroxide solution. They were analyzed by measuring the electrical conductivity change of the solution.

Results of these tests are presented in Table III, where columns 1, 2, and 3 show the wool manufacturer, filtering velocity, and average resistance at temperature indicated in column 7. Average inlet SO_2 concentration and efficiency are shown in columns 4 and 5 during length of test indicated in column 6. Material recovery factor shown in column 8 (A,%) is calculated from the product of average inlet concentration (in g./m.^{3}), air flow (m.^{3}/min.), time and filter efficiency (%): divided by the initial filter weight (dry). It represents the weight of gas removed by the filter as a per cent of initial weight (i.e. pounds of SO_2 removed/100 lb. of fiber).

Average efficiency of all filters tested dry was effectively zero. Wet filter tests showed significant positive efficiency in most cases. A typical room temperature test for Baldwin-Hill wool (from line 10 of Table III) is shown graphically in Fig. 1. Efficiency decreased from 37% to 23% during a period of 45 min. Filter resistance also decreased from 6.5 to 2 inches of water during the same period, due to the evaporation of residual moisture. Average efficiency is about 30% and average resistance is 4.2 in. of water during the test period. A similar test is shown for wet Mineralite wool at 170°F. in Fig. 2 (from one of the tests reported

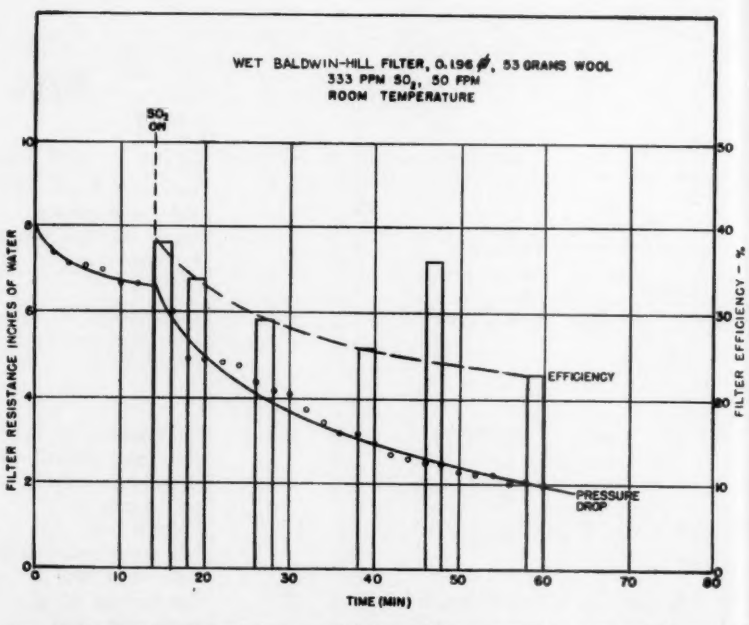

Fig. 1. Variation of wet slag wool filter efficiency (SO_2) and resistance with operating time (80°F.)

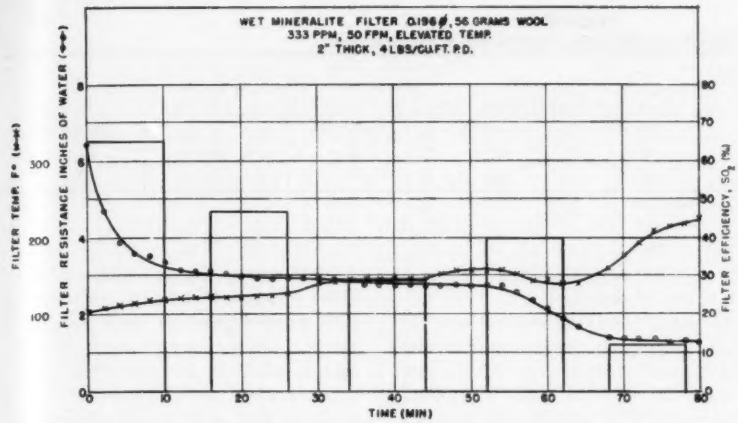
WET MINERALITE FILTER @196 ø, 56 GRAMS WOOL
333 PPM, 50 FPM, ELEVATED TEMP.
2" THICK, 4 LBS/CU.FT. P.D.
FILTER RESISTANCE INCHES OF WATER (++)
FILTER TEMP F° (++)
FILTER EFFICIENCY, SO2 (%)
TIME (MIN)

Fig. 2. Variation of wet slag wool filter efficiency (SO_2) and resistance with operating time (170°F.)

in line 4 of Table III). Filter efficiency decreased from 65% during the first 10 minutes to 12% during the last 10 minutes of the test period. Filter resistance also decreased from 6.5 in. of water initially to 1.3 in. of water finally, and the observed filter temperature (measured after the filter) increased as filter moisture evaporated and resistance decreased. Average efficiency was about 35% and average resistance was about 3.0 in. of water during a test period of 80 minutes, while the upstream gas temperature entering the filter was kept constant at 170°F.

Kaowool filters gave some indication of a slight positive efficiency when tested with residual moisture, but their resistance remained quite high during tests. No alteration of their physical condition was observed.

Both Mineralite and Baldwin-Hill filters had an average positive efficiency of about 25% when tested wet. For most wet tests with these two fibers, efficiency decreased steadily as the filter moisture evaporated. Initial efficiency for wet Baldwin-Hill filters was about 40% and for Mineralite filters was about 60%; in either case decreasing to zero in somewhat less than 2 hours, depending upon initial residual moisture (over which no control was maintained).

Although inlet SO_2 concentration and filtering velocity were varied over a reasonably wide range (from 110 to 400 ppm., and 50 to 150 fpm., respectively) no correlations can be made with filter efficiency because of the obscuring effect of larger changes depending upon moisture content.

Resistance to gas flow decreased with operating time (in the same manner as efficiency) as moisture was removed from the filter and became asymptotic to a minimum value represented by that of the dry bed (1 to 2 in. of water). Initial resistance for both slag wool filters ranged from about 6 to 12 in. of water, depending again upon residual interstitial moisture.

Wet Mineralite and Baldwin-Hill filters remove approximately 20 to 30% of SO_2 gas over most of the period while they are drying. Sulfur dioxide apparently reacts with material in the fibers, for filters tested were observed to have been attacked in the same manner as those observed during field studies mentioned previously. Upon drying, filters were bleached white and were powdery instead of fibrous. No tests were conducted to determine the "breakpoint" or total consumption of useable material in the fibers. All zero efficiencies obtained during these tests appeared to be due to a lack of sufficient moisture for complete reaction throughout the depth of the filter.

One laboratory test was conducted at 260°F. with a dry Baldwin-Hill filter that had been initially exposed to iron-oxide fume until its resistance had increased from 2.0 to 4.8 in. of water (line 6, Table III). This attempt to simulate field conditions gave essentially zero filter efficiency indicating that moisture is necessary for SO_2 removal. What effect the presence of iron-oxide and moisture have together was not investigated. Various metal oxides, among them iron-oxide, have been shown to catalyze the oxidation of SO_2 to SO_3 [4].

Sulfur dioxide samples were also taken during continuous field operation of a second Pilot Plant unit [5]. Filters were formed continuously by the slurry process, so that there was residual moisture present. Samples were analyzed by three different methods to evaluate the most useful one.

These tests indicated that the slag wool filter removed about 40 to 50% of SO_2 from an average of 75 ppm., in open hearth furnace gas, while performing its primary function as a particulate filter. Filters in the above tests were approximately 1 in. thick at 4 lb./ft.^{3} packing density, so that improved performance on the gas may have been possible with a thicker filter.

Average efficiencies obtained during field studies show variations similar to those observed in the laboratory which have been attributed to the presence or absence of significant interstitial moisture. Since average (positive) efficiency in field studies was about 50%, it is reasonable to assume that iron-oxide and other materials in open hearth fume can actually promote slightly higher collection efficiency for SO_2, even with the difficulties inherent in the comparison of field and laboratory information.

B. Nitrogen Dioxide (NO_2)

Various oxides of nitrogen are formed by fixation from the atmosphere in high temperature processes such as combustion and arc welding. Faith has presented the current status of pollution from nitrogen oxides in a recent publication [6]. Peters [7] has indicated that NO_2 hydrolyzes to nitric acid mist in the presence of water vapor. Absorption of NO_2 is controlled by the rate at which the gas phase reaction proceeds.

Mineralite slag wool filters were tested for NO_2 efficiency at 100 fpm filtering velocity at room temperature. Concentrations of NO_2 were established by metering commercial cylinder gas into the inlet duct of the test unit. Samples were collected in sintered glass absorbers containing sulfanilic acid and alphanaphthylamine solution[8] and the resulting color was measured in a colorimeter. Results are presented in Table IV (*see page 190*). Columns 1 to 3 give the average inlet concentration, and initial and final resistances, respectively. Average efficiencies for time periods 0 to 15, 15 to 45, and 45 to 80 min. are shown in columns 4 to 6. During 80 min. test runs, dry filters had an average efficiency of 10%. This val-

TABLE IV
Slag Wool Filter [a] Efficiency For Nitrogen Dioxide Gas

Av. Inlet Conc. ppm.	Resistance[b] Inches Water		Effic. During Period:			Av. Eff. %	Remarks
	Initial	Final	0-15 mm.	15-45 mm.	45-80 mm.		
30	0.45	0.48	11	12	8	10	Dry
35	1.28	0.94	27	22	35	28	Wet

a All filters 2 in. thick and 4 lb./ft.^{3} packing density, Mineralite fiber.
b At 100 fpm. filtering velocity, 70°F.

ue probably represents some contribution of interstitial moisture plus ambient atmospheric moisture content. Absolutely dry filters would be expected to give effectively zero removal.

Average wet filter efficiency was 28%. Moisture content of these filters was probably low, based on comparative initial wet filter resistance of 1.3 in. of water in NO_2 tests and 6.5 in. of water as found above in sulfur dioxide tests (Fig. 2).

C. Hydrochloric Acid (HCl)

Anhydrous and saturated hydrochloric acid gases were employed to evaluate Mineralite slag wool filters. Commercial anhydrous HCl (dry) was metered into the inlet of the test unit. Tests were made with saturated HCl by bubbling the dry cylinder gas through a wash bottle containing concentrated HCl. Samples were taken before and after the test filter with sintered glass gas absorbers containing demineralized water, and analyzed by measuring the electrical conductivity of the solution.

Results of these tests are presented in Table V. Columns 1 and 2 indicate the condition of the gas entering the test unit, and gas concentration, respectively, and columns 3 and 4 give initial and final filter resistance. The time variation of efficiency is included in columns 6 through 11 for 10 min. intervals, and average efficiency for the total time is given in column 12. Material recovered/unit weight of fiber (A,%) is presented in column 5.

Average inlet concentrations of about 1000 ppm. were used during anhydrous gas tests shown in lines 1 and 2. Filter efficiency ranged from 5 to 59% during 50 and 70 min. periods. Average removal efficiency for these tests was 26%. Filter resistance was relatively constant during testing at about 1.5 in. of water. A slight increase (on the order of 15%) was observed in one Test (line 2).

Line 3 presents results of a dry gas test when room moisture content was maintained greater than 85% R.H. Filter efficiency was significantly improved, the average value being increased to about 95%, at essentially no increase in filter resistance.

Two runs (lines 4 and 5) were made with the gas saturated by passing it through a wash bottle containing concentrated HCl, and then admitting it to the test unit. Average collection efficiency for these two tests was 78%, the range being 65 to 91%. Average gas concentration in these two tests was 640 ppm. (line 4) and 210 ppm. (line 5). Gas concentration varied during the test shown in line 5 from 57 to 670 ppm. From 0 to 10 min., concentration was 57 ppm.; from 10 to 20, 65 ppm.; from 20 to 30, 320 ppm.; from 30 to 40, 670 ppm.; from 40 to 50, 100 ppm.; and from 50 to 60, 78 ppm. Even with this greater than 10-fold range in gas concentration, filter efficiency is relatively constant, and more dependent upon length of service than concentration. For example, at 0 to 10 min. with a gas concentration of 57 ppm., efficiency is 85%, and at 20 to 30 min., with a gas concentration of 320 ppm. the efficiency is increased to 91%. At 50 to 60 min., with an inlet concentration of 78 ppm., efficiency has decreased to 65%. It may be concluded that efficiency will be dependent upon concentration and length of service. Life of the filter is decreased considerably at high concentrations. The filter in run 4 lasted only about one-half as long as that in run 5 which was tested at an average concentration less than half as high.

Moisture content of the entering gas stream is a significant factor in filter efficiency, as indicated by comparison of dry and saturated gas tests. The dry gas efficiencies probably reflect ambient moisture content during tests.

It was observed qualitatively at the completion of all tests that the filters felt moist, were bleached white, and apparently had reacted with the acid to form a powder (presumably $CaCl_2$) throughout the filter depth.

Alkalinity studies with HCl showed that Mineralite fiber will react with and neutralize about one-third (0.31) g. of acid/g. of wool. Maximum recovery of the 50 g. test pads would

TABLE V
Mineralite Slag Wool Filter [a] Efficiency For Hydrochloric Acid Gas

Gas[b]	Inlet Conc. ppm.	Resistance[c] Inches Water		A[d] %	Efficiency (%) During Period:						Av. Eff. %
		Initial	Final		0-10 m.	10-20 m.	20-30 m.	30-40 m.	40-50 m.	greater than 50 m.	
A	1000	1.60	1.63	35	59	24	34	36	21	27 [g]; 5 [h]	29
A	930	1.31	1.53	17	29	36	20	16	19	—	24
A[e]	400	1.49	1.49	31	94	97	96	95	91	—	95
S	640	1.44	1.63	27	90	81	66	—	—	—	79
S	210[f]	1.03	0.79	17	85	83	91	72	75	65 [g]	78

a Filter 2 in. thick, 3 lb./ft.^{3} packing density, dried before testing, Bethlehem Mineral Wool.
b A=anhydrous gas direct from cylinder; S=saturated gas generated by bubbling dry gas through conc. HCl.
c At 100 fpm. filtering velocity, room temperature.
d A=pounds of gas removed during test/100 lb. of fiber.
e Room moisture content greater than 85% R.H.
f Average gas concentration varied from 57 to 670 ppm. during test.
g 50-60 m.
h 60-70 m.

TABLE VI
Mineral Wool Filter Efficiency For Hydrofluoric Acid Gas

Wool[a]	Filt. Vel. fpm.	Inlet Conc. ppm.	Resistance[b] In. Water Initial	Resistance[b] In. Water Final	A[c] %	Efficiency (%) During Period (min.): 0-10	10-25	25-40	40-55	55-70	70-85	Min. Eff. %	Max. Time Min.
M (4)	80	390	0.8	1.4	13	80	78	65	65	40	23	0	120
M (4)	160	310	2.3	4.8	15	59	72	63	47	31	21	0	110
M[d] (5)	80	580	3.7	1.2	16	—	80	80	83	94	90	62	180
M[d] (5)	160	440	8.9	4.6	35	93	96	97	97	95	67	46	90
M[e] (3)	160	350	2.4	3.5	6	32	48	50	40	33	—	0	170
B-H (4)	80	490	1.2	2.1	9	65	69	60	45	31	29	12	135
B-H (4)	160	250	2.1	4.5	14	75	96	94	73	49	—	6	100
B-H[d] (5)	80	420	5.2	2.0	12	—	73	66	60	53	38	11	160
B-H[e] (4)	160	480	6.8	7.2	10	45	15	—	—	—	—	4	55
K-A (4)	80	260	4.2	0.2	4	48	67	33	—	—	—	9	80
K-A (3)	160	300	5.9	0.3	21	76	81	48	—	—	—	25	55
K-B (3)	80	480	2.5	0.8	7	48	33	—	—	—	—	6	30
K-B (4)	160	430	3.7	0.6	18	68	41	—	—	—	—	24	30

a All filters 2 in. thick, packing density (on dry basis) from 3 to 5 lb./ft.^{3} as indicated in parentheses. Wool tested: Mineralite (M), Baldwin-Hill (B-H), and Kaowool A (K-A) and B (K-B).
b At indicated filtering velocity, 70°F., except lines 5 and 9 at 500°F.
c Filter rating factor based on first 60 min. of test (prorated for shorter tests), lb. of acid recovered/100 lb. of fiber.
d Contained residual moisture from formation process at start of test.
e At 500°F.

be about 16 g. of acid before the total available alkalinity was consumed. This order of magnitude of acid was recovered by test filters in this study (from 8 to 14 g.), indicating most of the useful life had been expended in test periods of approximately 45 min. to one hr.

D. Hydrogen Fluoride (HF)

Gaseous and particulate fluoride compounds may be present in open hearth furnace gases when fluorspar (CaF_2) is used as a flux or when fluoride-bearing ores are used.

British experience indicates concentrations in the range of 0.1 gr./ft.^{3} probably as HF and SiF_4. Quantitative information on fluoride emission from open hearth furnaces in the United States was established by the U. S. Public Health Service survey in the Donora area, where a concentration of 0.008 gr./ft.^{3} of particulate fluoride compounds were found, with no evidence of injury to either humans or animals [9]. (See also Ref. 10).

As a part of studies on the use of mineral wool filters for collection of acid gases and mists, a number of tests were made with hydrogen fluoride gas. Mineral wools should be particularly effective as filters for fluoride compounds because the majority of the fiber material will be available for reaction. If slag wool is considered to be effectively 30% calcium silicate, then HF will react with both components to form calcium fluoride, silicon tetrafluoride, and water:

$$CaSiO_3 + 6HF \rightarrow CaF_2 + SiF_4 + 3H_2O$$

The water formed will hydrolyze SiF_4 to SiO_2 and an aqueous solution of HF. Probably all of the material within the fiber will react with HF, or the theoretical recovery factor (A.%) should be 100%. (Additional performance tests with the intermediate compound SiF_4 are discussed in the next section).

Anhydrous HF was supplied from a cylinder and metered through a polyethylene tubing flowmeter. Samples were collected in sintered glass absorbers (paraffin coated walls) containing water. The fluoride ion was determined by its bleaching action on ferric thiocyanate [8].

Filters made from Mineralite slag wool were tested dry and wet at room temperature with filtering velocities of 80 and 160 fpm., and at elevated temperature at 160 fpm. Results of these tests are summarized in Table VI, lines 1 through 5. Column 1 of Table VI indicates the wool tested, with its approximate packing density (pounds per cubic foot) in parentheses. Dry filters were about 2 in. thick and those tested with residual moisture about 1½ to 1¾ in. thick. Inlet acid gas concentration is given in column 3 and filtering velocity and resistance in columns 2 and 4, 5, respectively. Average inlet concentration ranged from about 300 to 600 ppm. Initial resistance of dry filters was 0.8 and 2.3 in. of water at filtering velocities of 80 and 160 fpm., respectively, and increased about two-fold during two hr. tests, due to the reaction of HF with material in the fibers.

Collection efficiency of Mineralite filters was observed to depend upon whether the filter surface was wet or dry. The variation of filter efficiency with operating life is given in columns 7 through 12 of Table VI. Fig. 3 is a plot of all tests made on Mineralite with HF gas, and in-

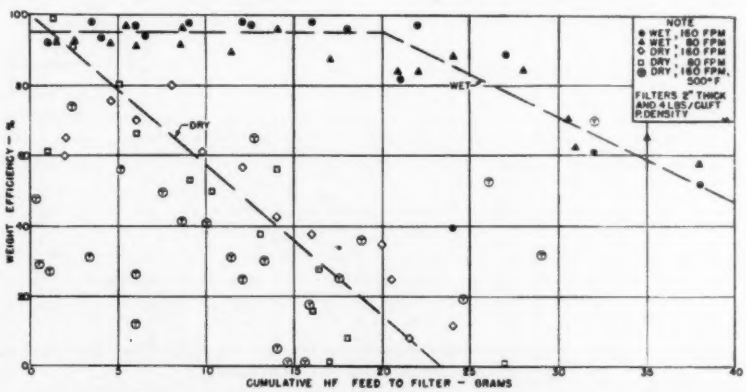

Fig. 3. Efficiency of Mineralite slag wool filters as a function of cumulative acid feed (HF)

dicates the above relationships. In the case of wet filters (the upper dotted line), efficiency remains reasonably constant at approximately 95% until 20 g. of HF had been fed to the filter and then decreased slowly to about 45% as cumulative acid feed increased to 40 g. (The dotted lines in Fig. 3 show approximate trends, and divide observations into two equal groups, *i.e.*, half of the data lie above and half below the dotted line).

There is a point of efficiency drop-off at about 20 g. of acid feed. This amount of acid is about 40% of the weight of the filter. Even after this point is passed, the reduction in efficiency is relatively gradual.

Resistance of initially wet filters decreased noticeably during tests as interstitial moisture evaporated (columns 4 and 5, and lines 3 and 4). Fig. 4 shows the variation in resistance for Mineralite slag wool filters as a function of cumulative hydrofluoric acid feed. Filters appeared to dry out during the period of time required for approximately 20 g. of HF to be fed into the system. At 80 fpm. filtering velocity, a change in slope appears at about 18 grams of acid fed, and at 160 fpm. the change in slope appears at about 22 g. These correspond in general to the location of the change in slope of the efficiency-acid feed curve for wet filters (Fig. 3). This correlation indicates that the presence of a significant amount of interstitial moisture is necessary for continued high efficiency removal.

Dry filters removed less HF and efficiency dropped to zero within a shorter time, as shown by the curve on the left of Fig. 3. (The dotted line for dry filters does not include data

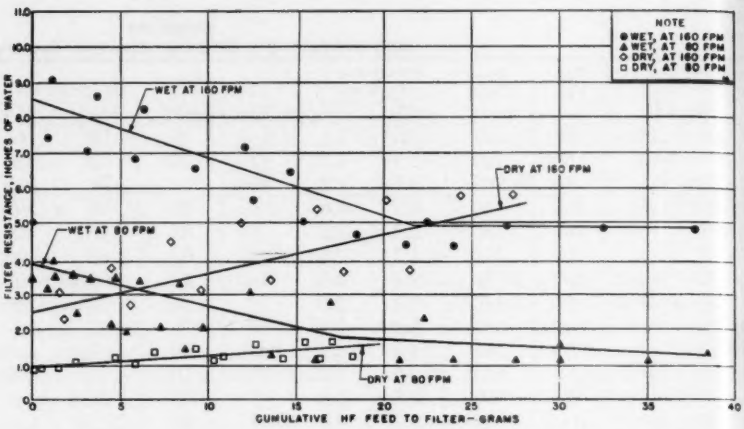

Fig. 4. Resistance of Mineralite slag wool filters as a function of cumulative acid feed (HF)

for tests made at 500°F., i.e., points marked with "T"). Efficiency falls from greater than 90% initially to zero at about 23 g. of acid feed. An efficiency of 80% is reached at about 5 g. of acid, or at 10% of filter weight. Tests were also made at 500°F. as indicated in Fig. 3. Efficiency of dry filters at high temperature was slightly less than at room temperature, with the majority of test points lying below the dry filter curve.

Baldwin-Hill filters were tested dry at 80 and 160 fpm. filtering velocity (room temperature); at 160 fpm exposed to 500°F. gas; and at 80 fpm with filter containing residual moisture (wet). A summary of these tests is presented in Table VI, lines 6 through 9. Average inlet HF gas concentration (column 3) ranged from 250 to 500 ppm. Resistances of dry filters average 1.2 and 2.1 in. of water initially at filtering velocities of 80 and 160 fpm. respectively, and increased to approximately twice these values during operation over a period of about two hr.

Efficiency of collection depends upon the amount of acid fed to the filter during operation, as shown in Fig. 5 (which is a plot of all tests made with Baldwin-Hill fiber on HF gas). Wet filters show a decreased efficiency (break-point) at about 10 g. of acid feed. During this initial period filter efficiency is relatively constant at about 91%. After passing the break-point, efficiency falls slowly to 19% at about 28 g. acid feed. The final section of the curve is in doubt, that is, data indicate positive efficiency (average 19%) at 32 and 34 g,. but the tendency to reach an asymptote is not clearly established. An efficiency of 80% occurs after 12.5 g. of acid feed, or at 25% of filter weight. This is about half (as is the break-point value) of the amount found for Mineralite fiber. Original investigations of alkalinity showed that one g. of Baldwin-Hill wool would neutralize less HCl and H_2SO_4 (0.23 and 0.29 g., respectively) than 1 g. of Mineralite wool (0.31 and 0.44 g., respectively), the alkalinity of Baldwin-Hill being about 30% lower. It is interesting to observe that the HF break-point occurs at a lower cumulative amount of acid with Baldwin-Hill wool. Based on fiber alkalinity studies, and Mineralite performance shown in Fig. 3, this break-point would have been expected to occur at about 70% of the value found for Mineralite, or at 14 g. The rather large influence of the initial amount of residual moisture in the filter probably overshadows the actual fiber alkalinity break-point.

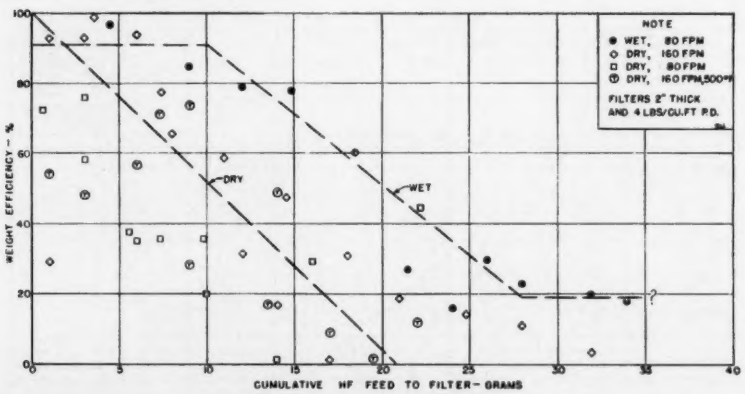

Fig. 5. Efficiency of Baldwin-Hill slag wool filters as a function of cumulative acid feed (HF)

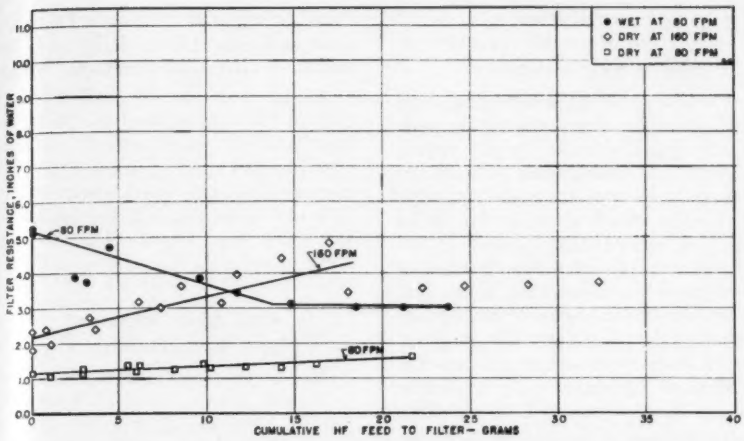
● WET AT 80 FPM
◇ DRY AT 160 FPM
□ DRY AT 80 FPM
FILTER RESISTANCE, INCHES OF WATER
80 FPM
160 FPM
80 FPM
CUMULATIVE HF FEED TO FILTER— GRAMS

Fig. 6. Resistance of Baldwin-Hill slag wool filters as a function of cumulative acid feed (HF)

Dry Baldwin-Hill filters show the same relationships as were determined for Mineralite. Efficiency is apparently inversely proportional to the cumulative acid feed, proceeding from nearly 100% initially, to zero at 21 g. acid feed. Performance of dry filters at 500°F. gas temperature is also plotted in Fig. 5 (points with a "T") and appears to follow the trend of dry filter performance, except that most efficiencies are lower than at room temperature. The effect of ambient atmospheric moisture content is apparent in these data.

Fig. 6 shows the variation of resistance for wet and dry Baldwin-Hill filters. It is again apparent that a change in slope of the "drying" filter resistance occurs at about 13 g. HF feed, or approximately in the same general relation to the change in slope of the efficiency curve as was found with Mineralite filters (Fig. 3 and 4). This again indicates the dependence of removal of HF on the amount of residual moisture present. Ambient moisture content also influences collection efficiency.

The initial assumption implied in the reaction of $CaSiO_3$ with HF, that sufficient water will be formed to hydrolyze all SiF_4 and prevent its escape is probably in error. During dry filter tests a wide scatter of points was observed (cf., Fig. 3 and 5) which probably reflect changes in moisture content in ambient air admitted to the test unit, and also the availability of water formed in the reaction. In either case, average efficiency of filters tested "dry" was significantly lower than those tested with residual moisture. This would indicate that a certain proportion of SiF_4 is escaping from the fiber bed. Unfortunately this was not subjected to test during these studies. Based upon the reaction, if 6 molecules of HF enter the test unit and four fluoride molecules are combined in each SiF_4, the lowest average efficiency that should be obtained is about 33% (assuming all HF entering is collected by fibers). A gross average taken from the left hand dotted lines in Fig. 3 and 5 would indicate that efficiency of dry beds was about 45%. Unknown variations in ambient and filter moistures prevent any more accurate analysis.

Subsequent tests of filters with controlled moisture content in the air passing to the filter have indicated that apparently a critical moisture exists below which little acid removal takes place. Saturated air (without actual liquid droplets) gave 95% removal on filters which would ordinarily be considered dry. This is in agreement with what is expected if sufficient moisture is present in the air stream and within the filter to prevent the SiF_4 from escaping as a gas.

Babcock and Wilcox Kaowool filters were tested dry (at room temperature) at 80 and 160 fpm filtering velocities, with results as indicated in Table VI, lines 10 through 13. Kaowool filter resistance decreased steadily from the start of exposure (columns 4 and 5). Initial resistance ranged from 2.5 to 5.9 in. of water and decreased to 0.8 to 0.3 in. of water, respectively at the conclusion of one-half to one and one-half hr. tests. Collection efficiency again is apparently inversely proportional to cumulative acid feed, as shown in Fig. 7. Dry filter efficiency was generally lower than found with the two slag wools, and also dropped about twice as rapidly. Zero efficiency occurred at approximately 10 g. of acid feed (or about half of the value found for the slag wools). (No tests were made with initially wet Kaowool). These kaolin wool filters were observed to have been very seriously attacked when removed from the test unit with large holes visible throughout the depth of the bed. Mineralite and Baldwin-Hill filters were bleached to a white and grayish-white color after reaction, but no holes were visible. Reaction oc-

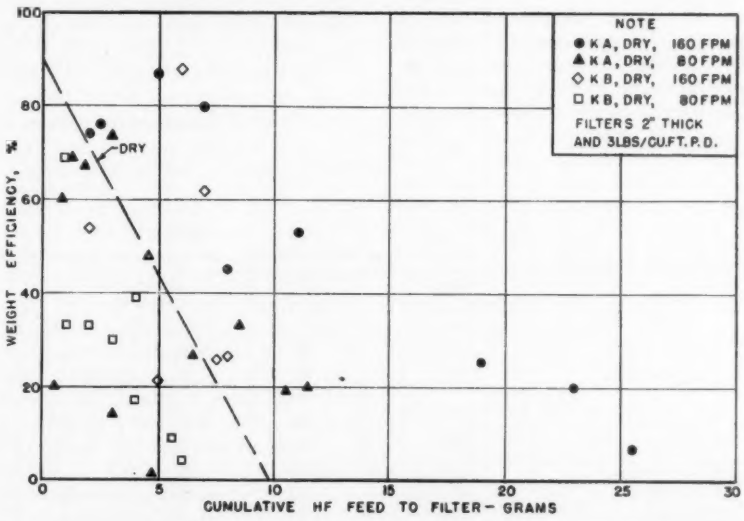
NOTE
● K A, DRY, 160 FPM
▲ K A, DRY, 80 FPM
◇ K B, DRY, 160 FPM
□ K B, DRY, 80 FPM
FILTERS 2" THICK
AND 3LBS/CU.FT. P.D.
DRY
WEIGHT EFFICIENCY, %
CUMULATIVE HF FEED TO FILTER— GRAMS

Fig. 7. Efficiency of Kaowool mineral wool filters as a function of cumulative acid feed (HF)

curred throughout the depth of the filter.

It may be concluded that collection efficiency for the three types of mineral wools tested on HF is a function of (a) whether the filter is initially dry or wet, (b) the cumulative amount of acid fed to the filter and (c) the absolute humidity of the entering air.

Resistance of dry Mineralite and Baldwin-Hill filters increased with exposure as a result of the HF reaction with the fibers. A powdery product was formed (CaF_2 and SiO_2 probably) which filled voids.

Kaowool filter resistance decreased continuously from the start of exposure. On removal from the test unit these filters felt wet and contained many holes.

Several tests were made at elevated temperature with Mineralite and Baldwin-Hill filters. They showed very little visible reaction. Apparently significant water is necessary and at 500°F. no water can remain on the filter fibers. At room temperature a certain amount of water does remain on the fibers and the reaction is quite rapid.

Two inch thick slag wool filters packed to a density of 3 to 5 lb./ft.^{3} will remove 90 to 95% of HF gas from an air stream (containing 250-600 ppm.) when sufficient moisture is present in the entering air to prevent SiF_4 from escaping as a gas.

E. Silicon Tetrafluoride Gas (SiF_4)

For tests with SiF_4, commercial cylinder gas was metered into the test unit. Because of the decomposition of silicon tetrafluoride in the presence of water vapor [11], samples were collected before and after the test filter with a Millipore filter followed by a sintered glass absorber.

Reactions probably occur as follows:

$$SiF_4 + 2H_20 \rightarrow SiO_2 \text{ (solid)} + HF \text{ (mist)}$$
$$2HF + SiF_4 \rightarrow H_2SiF_6$$

Formation of particulate SiO_2 from SiF_4 is easily demonstrated by passing the gas across the top of a beaker of water, or by exhaling through the gas as it escapes from the cylinder. A visible cloud of SiO_2 (or SiO_2x H_20) is immediately formed. In absorption of SiF_4 in water, the film of SiO_2 once formed, can act as an effective barrier to further absorption, particularly on water droplets in spray towers [11]. Although the formation of particulate SiO_2 is demonstrable in saturated gas, not enough is known about the intermediate reactions to predict the amount of particulate formed when the gas is not saturated [12].

Dry Mineralite filters were exposed to SiF_4 released in ambient air passing to the test unit and all results indicated essentially zero removal with gas concentrations of 100 to 420 ppm. Millipore filters were not used preceding the gas absorbers in this test, and it was observed that plugging of the sintered glass was occurring.

Another dry filter was placed in the test unit and nearly saturated air (95% RH) was used for testing. Collection efficiency of the filter was 100% based on amount of fluoride found in each absorber.

A test was also made with a wet Mineralite filter (with residual moisture from slurry formation) and a collection efficiency of 100% was obtained. It was apparent in this case that SiO_2 had formed on the filter which led to plugging and caused resistance to rise fairly rapidly.

The filtration (absorption) of SiF_4 with dry slag wool filters depends entirely upon the moisture content in the entering gas; for very low (normally ambient) values, efficiency of fluoride removal is negligible; for saturated gas (95% RH) the removal is effectively complete.

Actual reaction rate and distribution of SiO_2 throughout the test system was not quantitatively investigated in this study. Correlations with moisture content and penetration of SiO_2 should be made if the results of the above tests appear favorable for certain air pollution control applications.

Acid Mist Removal

A. Sulfuric Acid (H_2SO_4)

Wet slag wool filters were found to remove about 20 to 25% of SO_2 gas in controlled laboratory studies reported above. Absorption of the gas in water remaining in the filter from the forming process probably produces $CaSO_4$ on and within the fibers due to leaching of the flux. Tests were also conducted with H_2SO_4 mist to determine if its action on the fibers led to the type of attrition that was observed previously during field studies, and also to evaluate the performance of slag wool filters as a potential air pollution control method.

A first series of tests were made on Mineralite and Baldwin-Hill filters with sulfuric acid mist generated by dropping 50% acid on a heated plate (approximate particle size 0.7μ MMD[13]). Samples were collected up-and downstream of the test pad on Millipore filters and analyzed by titration with NaOH.

Results of these studies are presented in Table VII (lines 1 through 5). Columns 1 through 5 show the wool tested, average inlet concentration, filtering velocity, and initial and final resistance, respectively. Average efficiencies for the period 0 to 20 min. are given in column 6.

Baldwin-Hill filters tested at 50 and 100 fpm. velocity removed 65 and 73% of inlet concentrations of 500

TABLE VII

Slag Wool Filter [a] Efficiency For Sulfuric Acid Mist

Wool	Average Inlet Conc.[b] mg./m.3	Filt. Vel.[c] fpm.	Resistance[c] Inches Water		Efficiency During Period			Av. Eff.
			Initial	Final	0-20 m.	20-40 m.	40-60 m.	
Baldwin-Hill	500	50	0.35	0.35	65	—	—	65
Baldwin-Hill	2000	100	0.90	1.10	73	—	—	73
Mineralite	970	50	0.13	0.15	68	—	—	68
Mineralite	550	100	0.30	0.60	56	—	—	56
Mineralite	320	200	1.20	—	32	—	—	32
Mineralite	120	50	0.35	0.42	68	69	70	69
Mineralite	65	100	0.50	0.56	73	71	70	71

a All filters 2 in. thick and 4 lb./ft.^{3} packing density.
b 100 mg./m^3=25 ppm., H_2SO_4.
c At 70°F.

TABLE VIII

Slag Wool Filter [a] Efficiency For Sulfur Trioxide Mist

Average Inlet Conc.[b] mg./m.3	Resistance[c] Inches Water		Efficiency During Period:				Av. Eff.
	Initial	Final	0-25 m.	25-50 m.	50-75 m.	75-100 m.	
98	0.64	0.69	22	40	41	—	34
56	0.70	0.78	33	36	31	30	32
37	0.40	0.68	19	32	23	30	26

a All filters 2 in. thick and 4 lb./ft.^{3} packing density, Mineralite fiber.
b 100 mg./m.3=31 ppm., SO_3.
c At 100 fpm. filtering velocity, 70°F.

and 2000 mg./m.^{3}. Mineralite filters were tested at 50, 100 and 200 feet per minute filtering velocity (lines 3, 4 and 5) at constant inlet mass rate, and they removed 68, 56 and 32%, respectively.

Average collection efficiency was 52% for Baldwin-Hill filters and 69% for Mineralite filters. This exposure produced a condition identical to that observed on slag wool that had been used to filter open hearth stack gases during pilot plant field studies. The upstream face showed deterioration of fibers, and additional embrittlement was observed within the filter. It was concluded from these results that sulfur acid attack was the major cause of fiber attrition in field fume filtration tests.

Further acid mist removal studies were made to investigate useable life on Mineralite fiber filters. Mist was generated with a compressed air aspirator. Large droplets were removed by impingement on a baffle placed in front of the nozzle, and also by elutriation as the mist passed upward in the container [13] (approx. particle size 2.0μ MMD [14]). Samples were collected up-and downstream of the test filter on Millipore filters and analyzed by electrical conductivity.

Results of these tests are shown in Table VII (lines 6 and 7) and the efficiency is recorded as a function of time. Over a one hour period there was no serious loss in efficiency due to acid attack of the fibers. The filters, when removed, were observed to be in good condition with only slight attack visible at the upstream face. Qualitative observation indicated that only a small part of the fiber had reacted. Average filter efficiency during these tests (70%) was higher than found in the first group due to the larger particle diameter.

Since fiber alkalinity studies have indicated that Mineralite fibers neutralize about 0.4 g. of sulfuric acid/gram of wool, a calculation of the total amount of material collected by the filter is indicative of the relative amount of total possible acid recovery during these tests. In the last test (line 7) the initial filter weight was about 50 g. It was exposed to 20 ft.^{3} of air/min. (a 6 in. diam. filter at 100 fpm.). Total acid removed by the filter is 1.58g.

Fifty grams of fiber should be expected to neutralize a maximum of 0.4 x 50 = 20 g. of H_2SO_4 if all the available alkali was at the surface. The amount recovered of the possible total is then 7.9%, which agrees with the observation of the filter condition. On this basis maximum filter life would be about 10 to 15 hr. at this concentration.

The assumption that all fiber alkalinity is available for reaction may not be totally correct because mist deposition occurs at the fiber surface. A sulfate layer at the surface would interfere with further reaction and effectively reduce the total amount of material collected.

Higher concentrations may reduce total filter life in direct proportion to concentration. Higher efficiency can be obtained with a deeper filter bed, in accordance with the logarithmic penetration law and resistance would be expected to increase in proportion to bed length.

B. Sulfur Trioxide (SO_3)

Tests with sulfuric acid mist discussed above were made with relatively large particles. If the acid is formed from oxidation of sulfur at high temperature then the gaseous sulfur trioxide will absorb moisture from the air and form very small particles. An attempt was made to use catalytic conversion of SO_2 to SO_3 at 400°C. with vanadium pentoxide in a device similar to that of Gillespie [15] in order to generate small particles. Because of technical difficulties encountered with catalyst poisoning, this method was not used.

Sulfur trioxide generation was accomplished in preliminary equipment by oxidizing SO_2 gas with ozone. A stream of commercial oxygen (3 lpm) was passed through a small laboratory electrostatic precipitator (15 KV, AC) [16] where approximately 10% was found to be converted to ozone. The oxygen-ozone stream was then combined with SO_2 gas (0.05 lpm.), passed into a 40 l. carboy and then into a small bottle whose walls were moistened by blotters. From the total gas flow and carboy volume, residence time of 13 min. was allowed for conversion of SO_2 to SO_3. A white mist emerged from the outlet, indicating that the generation method was successful. To obtain the SO_3 free of residual SO_2, stiochiometric volumes were used, but variations in ozone production led to some doubt as to the complete oxidation of SO_2. A further acid gas absorbent would probably have been required. Efficiency of conversion was not determined. This method was therefore abandoned in favor of the one described below.

Tests of Mineralite fiber on SO_3 were made by gently heating fuming sulfuric acid and passing the vapor-mist combination through a large electrostatic precipitator to remove H_2SO_4 droplets. The gaseous SO_3 escaped and passed into the test unit, picking up moisture rapidly from dilution room air to form small droplets. From the work of Gillespie [15] it has ben shown that this occurs very rapidly (approximately 0.01 sec.) and that such particles are on the order of 0.5μ MMD. Samples were collected up-and downstream on Millipore filters followed by sintered glass absorbers containing water, and were analyzed by electrical conductivity.

Test results are given in Table VIII. Average collection efficiency of 2 in. thick filters was 31%, and no significant change in efficiency was observed during a continuous running period of 100 min. Efficiencies are lower than those for H_2SO_4 mist because of the smaller particle size. The total filter life can

be estimated from calculations; for example, at an average inlet concentration of 50 mg./m.³, filters were tested for about 100 minutes at an average efficiency of 31%, so amount of fiber used would be 4.4%.

Expected filter life at an average concentration of 50 mg./m.³ would be about 23 hr., or approximately twice as long as found during H_2SO_4 tests, where the concentration was 90 mg./m.³ (about twice as high). If sulfate forms on fiber surfaces as discussed above, and all available base is not used, the estimate given above may be too high.

C. *Nitric Acid (HNO_3)*

Mineralite slag wool filters were tested on nitric acid mist generated by dispersing concentrated HNO_3 (80%) with the same compressed air aspirator used for sulfuric acid mist. Samples were collected before and after the test filter on Millipore filters followed by sintered glass absorbers. Colorimetric analysis was made with the brucine reagent described by Snell [8].

Dry slag wool filters were tested at filtering velocities of 50, 100 and 150 fpm. at room temperature. Two runs were also made at room temperature and 100 fpm. velocity with filters that contained moisture remaining after partial drying. Two additional tests were made at gas temperature of 500°F. Results of these tests are given in Table IX.

Increased filter velocity makes a slight but significant increase in filter efficiency at constant inlet loading as seen by comparing the average efficiency at 50 fpm. (74%) with that at 150 fpm. (84%).

A two-fold increase in filter loading at constant velocity (lines 2 and 3) gives an improved efficiency (from 75 to 87%). The outlet concentration increased only slightly in this case, from 35 mg./m.³ to 40 mg./m.³

Filters tested with residual moisture (lines 5 and 6) showed a slightly lower average efficiency than dry tests at the same filtering velocity. Wet filters were observed to sag slightly away from the upper surface of the filter holder which could have caused peripheral leakage around the filter and lowered efficiency (average about 55%). The resistance of these filters fell during testing (columns 3 and 4) as interstitial moisture dried out.

Two tests at high temperature indicated slightly lower collection efficiency. This is either due to evaporation of mist droplets to a small size (or to the gas phase) or to the effects of high temperature on removal mechanisms.

The calculated filter rating factor indicated in Table IX (A, %; column 5) represents the amount of nitric acid mist the filter recovers per hundred pounds of slag wool. All filters tested at room temperature reacted with the acid to form a white powdery product (presumably calcium nitrate) on the upstream face for about the first half inch. Most measurements were for 1½ hr. with some extended to nearly 3 hr.

Fig. 8 (see page 197) shows the filter efficiency as a function of the cumulative amount of acid supplied to the system as calculated from the upstream concentration and operating time. Average efficiency of dry filters at room temperature is about 80% during the period when the total amount of entering material is less than about 10 g. as indicated by the left portion of the dotted line. There is some tendency for filter efficiency to decrease slightly during this period. Beyond 10 g., the efficiency seems to fall off rather more rapidly, as indicated by the right portion of the dotted line.

Filters used during these tests weighed 50 g. and seemed to filter effectively about 0.2 g. of nitric acid/g. of wool before a marked decrease in efficiency occurred. This checks approximately the values found for sulfuric and hydrochloric acids by direct titration (0.3 g. of acid/g. of wool). No dry filters were tested beyond about 13 g. acid feed, but one wet filter was tested to 22.2 and 25.2 g., efficiencies at these points being 49 and 51%, respectively, as indicated by small open circles at the extreme right of Fig. 8. It is reasonable to assume that although efficiency starts to decline at about 10 g. acid feed, it does not go immediately to zero but may approach this value asymptotically due to the physical characteristics of the reaction products of the slag wool and the acid.

Filter rating factors ranged from

TABLE IX

Slag Wool Filter [a] Efficiency For Nitric Acid Mist

Filt. Vel. fpm.	Av. Inlet Conc.[b] mg./m.3	Resistance[c] Inches Water Final	Initial	A[d] %	Efficiency (%) During Period: 0-20 m.	20-40 m.	40-60 m.	60-80 m.	Greater Than 80 m.	Av. Eff.	No. of Tests
50	125	0.30	0.43	5	70	81	77	79	66 [g]	74	2
100	140	0.49	0.72	9	80	72	76	71	70 [h]	75	3
100	310	0.53	0.81	22	82	94	72	54	—	87	1
150	140	0.98	1.25	13	90	91	80	56	—	84	2
100[e]	235	0.95	0.57	9	41	42	54	68	—	49	1
100[e]	315	0.83	0.41	17	—	80	63	51	50 [k]	60	1
100[f]	—	1.28	1.28	—	42	45	79	68	—	58	2

a All filters 2 in. thick and 4 lb./ft.³ packing density, Mineralite fiber.
b 100 mg./m³ = 39 ppm., HNO_3.
c At indicated filtering velocity, 70°F., except line 7 at 500°F.
d Filter rating factor based on first 80 min. of test, pounds of material collected per 100 pounds of slag wool, calculated from inlet mist loading (L), flow rate (Q), time exposed (T), filter efficiency (E) and initial weight of filter (W): A = LQTE/W, expressed as %.
e Filter contained residual moisture from formation process at start of test.
f At 500°F.
g At 110 min.
h At 170 min.
k At 150 min.

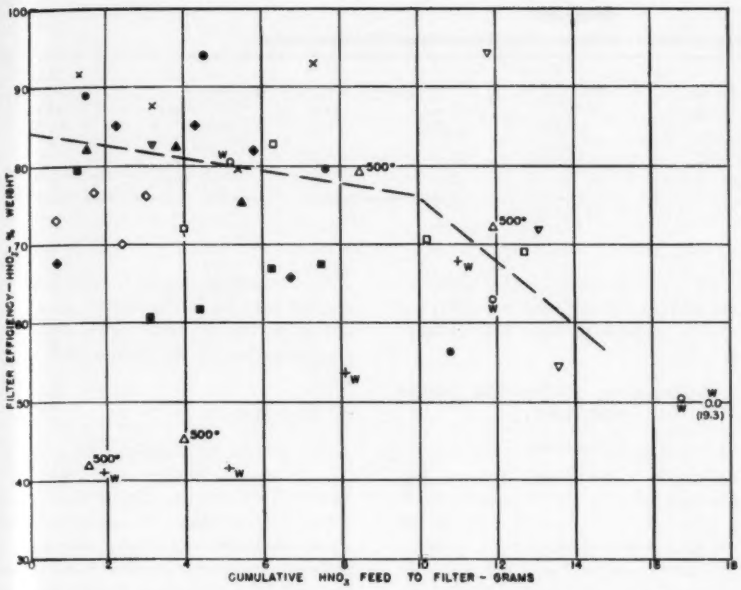

Fig. 8. Efficiency of slag wool filters as a function of cumulative nitric acid feed.

5 to 13% with an average inlet loading of 134 mg./m.^{3} of mist, based upon the first 80 min. of test. This agrees well with the data given in Fig. 8 for the initial period of test when efficiency is relatively constant at 80%. During this time the filter actually recovers 8 g. of acid which is equivalent to an average "A" factor of 16%. The "A" factor increased slightly with an increased filtering velocity (lines 1, 2 and 4, Table IX). Higher inlet concentration and higher filtering velocity also produce improved collection efficiency.

D. Phosphoric Acid Mist (H_3PO_4)

Phosphoric acid mist was generated by subliming solid phosphorous pentoxide (P_2O_5) at 205°C. and passing the vapor through water to form a mist. Isokinetic samples were collected with Millipore filters up-and downstream of the test filter and analyzed by electrical conductivity (in a water solution).

Mists prepared from the sublimation of phosphorous pentoxide in a saturated atmosphere were measured by Gillespie and found to be about 1.5μ MMD [15].

Results of efficiency tests are shown in Table X. The first three columns give the inlet mist concentration and initial and final filter resistance, respectively. During test periods of from 2 to 4 hr., average filter resistance remained very nearly constant in each test. Average inlet concentrations ranged from 44 to 108 mg./m.^{3} during the same period. Average hourly efficiency is given in columns 5 to 9. There is a definite decrease in efficiency with operating time apparent in each test. Average efficiency for all tests was 71%; individual values ranging from 8 to 94%.

Filter recovery factor, "A" (%) is given in Column 4, as calculated from total material feed and efficiency, divided by initial filter weight. Values shown are for the first hour of testing in the first 3 lines, and for 35 min. in line 4. Average recovery is about 5% for the indicated figures. Additional calculations of the "A" factor were made for each test at the completion of the run. These values are: line 1, 5% at 112 min.; line 2, 6% at 171 min.; line 3, 19% at 235 min.; and line 4, 26% at 257 min. There is an increase in recovery approximately in proportion to the increase in operating time. In line 2, "A" was 3% at 60 min., and is 6% at 171 min.; or a two-fold increase in "A" for a tripling of time. The amount of material recovered would be expected to increase in the same proportion as time if efficiency and inlet concentration remained constant. Differences in this relationship are explained, in the case of line 2, as due to a decrease in filter efficiency (i.e. less material recovered/unit time as time increased) and decreased inlet concentration. In line 3, "A" was 5% at 60 min., and 19% at 235 min., or the increase in "A" (19/5 = 3.8) is almost exactly the same as the increase in operating time (235/60 = 3.9). This would also be expected from the relatively constant efficiency during the four hour period. Values of "A" did not correlate as well with operating time in tests on lines 1 and 4.

Fume Removal

A. Iron Oxide (Fe_2O_3)

The use of slag wool filters for recovery of iron oxide fume from 1000°F. open hearth furnace gases has been reported in detail elsewhere [1, 2]. To summarize these studies briefly, it was found that 2 in. thick filters with a packing density of 5 lb./ft.^{3} would remove about 90 to 95% of the fume generated by combustion of iron pentacarbonyl (in laboratory studies) and approximately the same amount of actual open hearth fume (in field studies). At 100 fpm. air velocity, initial filter resistance was about 1.5 to 2.0 in. of

TABLE X

Mineralite Slag Wool Filter [a] Efficiency For Phosphoric Acid Mist

Inlet Conc. mg./m.^{3}	Resistance[b] Inches Water		A,[c] %	Average Efficiency (%) During Period:				Greater Than 240 m.	Av. Eff. %
	Initial	Final		0-60 m.	60-120 m.	120-180 m.	180-240 m.		
44	1.35	1.37	4	71	70	—	—	—	71
44	1.31	1.37	3	82	65	25	—	—	55
92	1.35	1.45	5	84	58	76	72	—	73
108	1.20	1.21	8	88	85	87	84	81 [d]	85

a Filters 2 in. thick, 3 lb./ft.^{3} packing density, dried before testing, Bethlehem Mineral Wool.
b At 100 fpm. filtering velocity, room temperature.
c A = lb. of acid mist collected/100 lb. of fiber. Values reported for first three tests calculated for 0-60 min. period, last test for 0-35 min.
d 240-257 min.

TABLE XI

Mineralite Slag Wool Filter [a] Efficiency For Ammonium Bifluoride Fume

Inlet Conc. gr./ft.³	Resistance [b] In. Water		Increase In. H_2O/min.	A[c] %	Efficiency (%) During Period:			Run Time, Min.
	Initial	Final			0-20 m.	20-40 m.	40-60 m.	
0.15	1.05	1.57	0.023	—	98	—	—	15
0.20	1.22	4.72	0.077	20	99	99.8	—	38
0.15	1.81	7.86	0.116	21	98	99	99.8	59

a Filters 2 in. thick, 3 lb./ft.³ packing density, dried before testing, Bethlehem Mineral Wool.
b At 100 fpm. filtering velocity, room temperature.
c A=lb. of fume removed/100 lb. of fiber.

water at room temperature. Higher gas temperatures create higher flow resistance because of increases in gas viscosity (by approximately the 2/3rds power of the absolute temperature). Filters recover approximately 0.2 lb. of laboratory fume simulant/100 lb. of fiber/inch increase in filter resistance and 2.1 lb. of actual open hearth fume/100 lb. of wool /inch increase in resistance. The larger values found in field studies have been reconfirmed during more recent tests [5], and are probably due to the larger mean particle size and wider dispersion of sizes apparent in actual open hearth effluents. It was found that filters could be washed in water to remove accumulated fume, reconstituted, and reused for about ten times in laboratory studies, and about eight times in field studies. (The observable decrease in filter life during field tests is due to acid attack discussed in sections above). This method of washing and reusing filters means that each 100 lb. of fiber will recover 17 lb. of open hearth fume per inch increase in resistance, or for a 2 in. increase as allowed in field pilot plant units, each unit weight of fiber will recover about 1/3 of its own weight in fume before becoming unuseable. Filter resistance increased at the rate of 0.2 in. of water/minute with stationary filters exposed to an average inlet fume loading of 0.1 gr./ft.³ (Use of agglomeration devices preceding the stationary filter reduced the rate of resistance increase by about 30% [5]). A filter resistance increase of 2 in. of water requires about 10 min. under the stated conditions. Useable life of a given filter bed on actual open hearth fume is therefore about 80 min., or (24 x 60/80) 18 "volumes" of slag wool (within the filter) are requires per day. Volume of slag wool within the filter can be calculated from gas flow rate (in cubic feet per minute) and filtering velocity (100 fpm. in these tests), assuming a filter thickness. Total weight of filter material can be calculated from volume required and packing density. Based on this calculation, 50,000 cfm. of open hearth furnace gas (at 500°F.) requires approximately 3½ tons of wool/day.

B. Ammonium Bifluoride Fume (NH_4F-HF)

Reagent grade solid ammonium bifluoride was sublimed from a hot plate into the air stream leading to the test filter where it condensed as a solid. Up-and downstream samples were taken isokinetically and collected in 15 KV AC precipitators [16]. Fume was washed from the precipitators and analyzed by its bleaching effect on ferric thiocyanate [8].

These results are presented in Table XI. Average inlet fume concentration is indicated in column 1. The range of concentrations extended from 0.15 to 0.25 gr./ft.³ Particle size of fume produced in a similar generator has been reported to be 0.54μ MMD [13].

Columns 2, 3 and 4 give the initial and final filter resistance, and rate of resistance increase, respectively. Average initial resistance of all filters was about 1.36 in. of water. Resistance rate increased from 0.02 to 0.1 in. of water/min. as test length was extended from 15 to 59 min., indicating the initial increase is relatively slow but as the filter plugs and resistance rises, the rate of increase of resistance becomes exponentially larger.

Filter efficiency is indicated in columns 6, 7 and 8 as a function of operating time. It increased somewhat with length of run and was observed to be greater than about 98% for every test. Fume recovery indicated in column 5, expresesd as per cent of initial weight of filter bed, was constant at about 20%.

Qualitatively, test filters appeared to have undergone chemical reaction for about 1/4 in. in from the upstream face, the reaction product being white, powdery and caked fairly stiffly.

Based upon the tests above, it is possible to remove greater than 98% of NH_4F-HF fume with a relatively thin mineral wool filter. The initial filter resistance would be expected to double due to accumulated fume in about 20 to 30 min. with an inlet concentration in the range of 0.1 gr./ft.³.

C. Fly Ash

Fly ash is technically not a fume by definition (fumes are generally below 1μ diam.). Because of the interesting possibilities for use of slag wool filters on incinerator and boiler effluents containing suspended solid and liquid particulate materials and gases, a number of tests were made with resuspended and freshly-generated fly ash.

Slag wool filters were tested with the National Bureau of Standards test dust which is a Cottrell precipitated fly ash resuspended with a compressed air jet. Mass median diameter of this test aerosol is about 15μ. Efficiency of Mineralite filters tested on the cold (room temperature) resuspension was determined by passing the aerosol through the filter and then through a Type S pleated respirator filter. Total weight collected on the slag wool filter was divided by the sum of the weights collected on both to calculate removal efficiency. Results of these tests are presented in Table XII.

Various thicknesses and packing densities were tested. particularly those found suitable for iron oxide filtration. One inch thick filters had average efficiency of 84 and 92% for 5 and 10 lb./ft.³ packing densities, respectively. Two inch filters tested on fly ash had average efficiences of 87 and 96% at densities of 2.5 and 5 lb./ft.³, respectively. This compares with approximately 90% for 2 in. 5 lb. filters tested on iron oxide.

The filter rating factor for fly ash ($B/\Delta p$, based on measured weight gain, %) indicates that slag wool will collect from 7 to 81% of its own weight/inch increase in resistance. For 1 in. filters, $B/\Delta p$ averages 55, 30 and 7% for 3, 5 and 10 lb. densities. Two inch filters had recovery factors of 72 and 12%/in.

TABLE XII

Efficiency of Mineralite Slag Wool Filters on Resuspended NBS Fly Ash

Filter Thickness In.[a]	Filtering Velocity fpm.	Av Fly Ash Conc. gr./ft.³	Av. Resistance in. w.g.			Av. Operating Time min.	Av. Efficiency %	B%[b]	B/Δp
			Initial	Final	Δp				
1	150	0.068	1.00	1.94	0.94	139	83	52	55
1 (5)	150	0.066	1.48	2.35	0.87	97	84	26	30
1 (10)	150	0.062	3.80	6.30	2.50	128	92	18	7
2 (2.5)	150	0.064	0.91	1.34	0.43	118	87	31	72
2 (5)	150	0.066	2.74	5.00	2.26	181	96	28	12
1	170	0.100	1.13	2.13	1.00	68	88	52	52
1	210	0.068	1.22	1.58	0.36	56	69	29	81
1	235	0.094	1.89	3.09	1.20	52	81	51	42
1	275	0.095	2.50	3.30	0.80	28	68	26	32
1	300	0.200	2.36	4.17	1.81	30	76	87	48
1	330	0.078	3.12	3.67	0.55	18	60	16	29
1	500	0.160	4.12	7.36	3.24	19	59	50	15

a Three lb./ft.³ packing density except as indicated, other densities shown in parentheses.
b Fly ash collected/initial filter weight, by weighing, (expressed as %).

increase in resistance. B/Δp was found to decrease with increased filtering velocity, from 55 pounds of fly ash/100 lb. of wool,/inch resistance increase, at 150 fpm., to 15 at 500 fpm. (This agrees with expectation, based on the Kozeny concept of porosity and the assumption that increased velocity will produce a lower porosity in the deposited material). Values of filter rating factor are considerably greater for fly ash than for iron oxide, which is presumably due to larger particle size in the fly ash.

Filters which had been exposed to fly ash were easily returned to their initial weight and resistances by reslurrying and rinsing. No fiber breakage was observed in these studies probably due to absence of sulfur gases.

Since resuspended ash has been shown to contain many agglomerates [17] it was felt that an actual test was desirable on the products of combustion of pulverized coal. This would be more indicative of particle size and performance expected from actual coal-burning installations.

Efficiency of Mineralite slag wool filters was therefore determined on fly ash generated by burning pulverized coal in an oxygen-air-gas flame. Pulverized coal (40 mesh) was aspirated into the compressed air stream feeding an air-gas burner. An 18 in. long by 2 in. diam. combustion chamber was used to mix the air-gas flame and a separate stream of oxygen. Oxygen was preheated by passing it through a pipe coil wrapped around the outside of the combustion chamber. Particle size of ash from a similar generator was 8.0μ MMD.

Filters used to determine up-and downstream concentration were MSA 1106B all glass paper held in probes described previously.[1] Binder added during manufacture was burned out before weighing the filters by heating them to 500°F. for 30 min. Data reported in Table XIII shows total aerosol and fly ash concentrations. Fly ash concentration was obtained by heating the final samples on the filter papers at red heat for 30 min. and then reweighing.

The filter types tested were those previously found most promising for open hearth furnace use, *i.e.*, 1 in. thick by 3, 5 and 10 lb./ft.³ density and 2 in. thick by 3 and 5 lb. density. Table XIII shows that the efficiency of the 1-3, 1-5, and 1-10 filters was 94, 99, and 99% respectively. The 2-3 and 2-5 filters were 94 and 95%, respectively. These efficiencies are slightly higher than the comparable filters tested against NBS redispersed fly ash.

An examination of Table XIII indicates that the efficiency of the total aerosol (unburned coal plus fly ash) is higher than the efficiency for fly ash alone. The coal should have a significantly larger particle size than the fly ash, so the reported efficiencies are indicative of the degree of combustion achieved in the burner.

The "A" values and "A/Δp" values of the tested filters are reported in terms of the total upstream aerosol concentration. Exposed to freshly formed fly ash, the 1-3, 1-5, and 1-10 filters have A/Δp values of 3.8, 1.7, and 1.3, respectively. The 2-3 and 2-5 filters have A/Δp values of 2.3 and 2.6, respectively. These

TABLE XIII

Results of Freshly-Formed Fly Ash Tests On Mineralite Slag Wool Filters

Filter Characteristics		Face Vel. fpm.	Temp. °F.	Length of Run Min.	Upstream Concentration gr./ft.³		Volatiles %	Initial Δp In. H_2O	Increase Δp In. H_2O	Total Eff.[a] %	Fly Ash Eff.[a] %	Total A%	A/Δp %/ In. H_2O
Thickness	Density lb./ft.³				Total	Fly Ash							
1 in.	3	147	550	36	0.026	0.012	54	1.2	1.4	97	93	4.3	3.0
		135	460	39	0.019	0.0061	68	1.0	0.6	96	93	2.6	4.6
1 in.	5	129	435	43	0.017	0.0063	65	2.3	0.7	98	99	1.8	2.5
		129	405	45	0.027	0.0091	—	2.6	3.0	99	99	2.9	0.9
1 in.	10	134	475	30	0.040	0.011	75	2.7	1.1	98	95	1.8	1.6
		127	415	35	0.033	0.011	—	4.5	1.5	99	98	1.5	1.0
2 in.	3	122	405	20	0.022	0.0075	—	1.4	0.4	98	94	0.95	2.3
2 in.	5	134	410	32	0.029	0.010	65	1.9	0.4	98	94	1.2	3.0
		127	365	40	0.026	0.0058	78	2.1	0.6	99	96	1.4	2.3

a Gravimetric.

are lower than the respective B/Δp values reported for the NBS fly ash and higher than the A/Δp values reported for the FE_2O_3 aerosol. This is indicative that the effective particle size of the freshly-formed fly ash lies between the two.

Removal Mechanisms

Previous sections have presented experimental results on the collection of various acid gases, mists and fumes with fiber filters of three types of mineral wools. For the most part, studies have been concentrated on the performance of Mineralite (Bethlehem Mineral Wool) since it represents a typical blast furnace slag wool of composition most likely to be duplicated in insulating wool plants. We have not attempted to alter the fiber composition to make its acid collection more favorable. At least two methods of producing better wool for collection of acid gases and mists can be achieved with present equipment and technology. The wool can be made with a higher proportion of basic flux, or it could conceivably be washed, coated, or sprayed with a basic solution after manufacture, so that each fiber carries an additional layer of material which neutralizes the particular acid under consideration. Since each pound of wool has an area of 1800 ft.^{2} available for gas and mist collection, the use of this method should permit a high acid recovery/unit of weight.

A. Filtration of Aerosols

Removal of solid or liquid particles from gas in fiber filters usually occurs by impaction, interception, or diffusion. Representative test results given in previous sections were correlated with the impaction parameter [18] and the relationship shown in Fig. 9 was obtained. Points calculated from tests on acid mists lie reasonably close to a straight line with a negative slope, indicating a decrease in filter penetration with increased particle size in accordance with impaction theory. Iron oxide and ammonium bifluoride fumes show considerably higher efficiencies that would be predicted from their impaction parameters. Fly ash results lie on either side of the extrapolated impaction line.

Acid mist particles are spherical and would be expected to show a correlation with the impaction parameter. In addition, when these droplets strike a filter fiber they presumably flow and proceed to lose

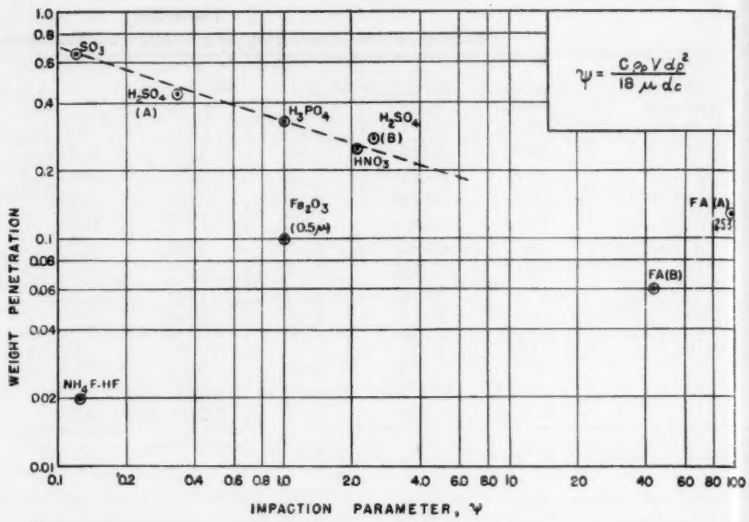

Fig. 9. Correlation of slag wool filter performance for acid mists and fumes as a function of inertial removal

their form, so that the filter would not have an immediate tendency to become clogged due to deposited aerosol particles.

Freshly-formed fumes, on the other hand, will generally produce a loose chain-like aggregate without any regular geometric shape. It is not unusual to find that fumes do not follow a close correlation with impaction theory, since the description of particle shape and size is mathematically difficult. Also, as fume particles deposit on filter fibers, a layer of material accumulates which changes the dimensions of the collecting fiber, and, in the extreme case when the layer is thick, the filtration will occur within the deposited layer to give high collection efficiency without regard to the nature of the original supporting fiber. During the generation of fumes, significant electrical forces are present which cause the chaining mentioned above, and these electrostatic forces also operate to produce increased efficiency.

It is expected that fly ash collection will be improved, above that by impaction alone, due to direct interception, which apparently is the case for Fly Ash (B). The lower efficiency found for Fly Ash (A) is attributed to lowered accuracy in the analytical method used to determine upstream concentration in this case (where the whole filter was weighed after exposure).

In order to predict mineral wool filter efficiency for an acid mist similar to those investigated, calculate the impaction parameter as shown in Fig. 9, and find the penetration from the experimental correlation shown for 2 in. thick, 4 lb./ft.^{3} beds. To predict necessary bed length for any other efficiency, proceed as outlined below.

It can be shown (See Ref. 19, page 121) for homogeneous aerosol particles passing through multiple layers of a fiber filter that a certain fraction of these particles will be removed in each successive layer. For example, if a given thickness removes 50% then a second layer of the same thickness (with all other characteristics the same) will remove 50% of what remains, and so on for each layer beyond. The overall efficiency of the filter can then be expressed as:

$E = 1 - e^{-sd}$

where: E = overall collection efficiency of the filter

e = 2.718 . . . the Naperian base

s = collection coefficient, a function of bed porosity, filter velocity, etc.

d = bed length

For example, in collection of sulfuric acid mist discussed above, the aerosol is not perfectly homogeneous, but the formula above will permit estimation of the required length of bed for various efficiencies. It was determined by test that a 2 in. layer of slag wool at a packing density of 4 lb./cubic foot would remove 70% of sulfuric acid mist. To determine the bed length required for 95% removal (assuming the same packing density), calculate the collection coefficient first, letting d = 1, (*i.e.*, unit length):

$E = 1 - e^{-sd} = 0.70$

$e^{-S(d)} = 0.30$

$-Sd \ (\ln e) = \ln 0.30$ (Since $\ln e = 1$)

$-Sd = -1.2$

$S = 1.2$

Knowing the coefficient, it is now possible to calculate bed length required for any other efficiency, for example, 95%:

$E = 1 - e^{-S(d)}$

$0.95 = 1 - e^{-1.2(d)}$

$e^{-1.2(d)} = 0.05$

$-1.2(d) \ (\ln e) = \ln 0.05$

$-1.2(d) = -3$

$d = 3/1.2 = 2.5$

Thus 2½ thicknesses of bed remove approximately 95% of the mist. The actual length, d, used in tests was 2 in., therefore, total bed length is 2x2.5=5 in. Initial resistance of this filter can be calculated from:

$R = KVd$

where:

R=total resistance, in. of water

K=a constant, in. of water/fpm. velocity/in. of bed length

V=filter velocity, fpm.

This relationship has been established for slag wool filters in previous investigations [20]. Resistance of 2 in. filters at 100 fpm. filtering velocity usually ranges from 1.0 to 2.0 inches of water, although it was somewhat lower in Table VII. Resistance of a 5 inch filter would therefore be approximately (2.5x1.0) 2.5 in. of water.

Similar calculations can be made for collection of other particulate materials, if one test has been made to establish the coefficient and the filter resistance at a known velocity.

B. Absorption of Soluble Acid Gases

Removal of soluble acid gases with slag wool filters has been shown to depend upon the residual moisture contained within the filter, and to a lesser degree upon the moisture content of the carrying gas. The exact relationship between the quantity of water present and the amount of gas removed was not firmly established. Since water is necessary for significant collection, absorption or solution of the soluble gas takes place in liquid films within the interstices of, and on the fibers. The principal resistance to gas transfer to a water film on the fibers is, as a first approximation, proportional to the rate of diffusion of the gas molecules through a thin stagnant layer of air surrounding the fiber. We can assume the liquid film surrounding slag wool fibers contains a certain concentration of basic material (CaO, NaO, etc.) and that chemical reaction prevents a substantial back-pressure from developing in the liquid phase (the liquid film resistance is probably negligible). In certain special cases the removal by a given filter may be governed by the rate of chemical reaction either in the gas or liquid films. This has been shown to be the case for NO_2 gas[7].

If a slag wool filter is kept continuously moist by fine sprays so that an assumption of continuity in the removal process could be used, it would be possible to calculate removal efficiency by standard mass transfer equations. Filters tested in this study were placed in the gas stream wet and allowed to dry while absorption was occurring, so that partial pressures in the solute were continuously changing and equilibrium values cannot be assumed. Possibly batch calculations could be employed to analyze data obtained in this study, to be useful in practical applications, some continuous moisturizing is required. With a known moisture rate, equilibrium values could be calculated.

Summary and Conclusions

Investigations of acid gas, mist and fume removal with mineral wool filters have indicated that two in. thick filters at four lb./ft.³ packing density will remove up to 80% of acid mist and up to 99% of acid gases and fumes. Total filter life depends upon concentration of contaminant in the entering air. A summary of filter performance is given in Table XIV. Estimated operating life based upon one use of the filter material can be obtained from data in Tables III to XIII. With particulates such as iron oxide and fly ash, it has been found possible to wash and reuse filters about ten times. When iron oxide was collected simultaneously with SO_2, filters were reused about eight times.

Particulate mist and fume collection takes place by impaction, interception and diffusion, depending on

TABLE XIV

Summary of Acid Gas, Mist, and Fume Test Results On Mineral Wool Filters[a]

Wool	Acid Gas	Acid Mist	Fume	Approx. Loading	Approx. Av. Eff.
M	SO_2	—	—	300 ppm.	25% (w)
	NO_2	—	—	35	28 (w)
	HCl	—	—	600	80 (w)
	HF	—	—	400	95 (w)
	SiF_4	—	—	400	99 (w)
	—	H_2SO_4	—	300 mg./m³	70 (d)
	—	SO_3	—	50	31 (d)
	—	HNO_3	—	200	80 (d)
	—	H_3PO_4	—	100	80 (d)
	—	—	Fe_2O_3	0.1 gr./ft.³	90 (d)
	—	—	$NH_4F.HF$	0.2	99 (d)
	—	—	Fly Ash	0.07	99 (d)
B-H	SO_2	—	—	300 ppm.	25% (w)
	HF	—	—	400	60 (w)
	—	H_2SO_4	—	1000 mg./m.³	70 (d)
KA	SO_2	—	—	300 ppm.	25% (w)
	HF	—	—	300	60 (d)
KB	SO_2	—	—	300 ppm.	20% (w)
	HF	—	—	450	50 (d)

a Average velocity 100 fpm. filter thickness 2 in., packing density 4 lb./ft.³. (w) indicates wet filter test result, and (d) dry.

particle size. Acid gas collection is significantly improved by the presence of moisture on slag wool filters. Absorption occurs in the moisture on the fibers and neutralization takes place in the alkali obtained by leaching the flux from the fibers. Fluoride collection is due to alkali neutralization and also by direct reaction of acids with silicates in the fiber.

Mineral wool filters have several features that are applicable to simultaneous collection of acid gases, mists, and fumes. Low cost (about 1¢/lb.), small fiber diameter (4μ) and ability to withstand high temperatures (1000°F.), are desirable for removal of submicron particles from industrial effluents such as incinerators and furnaces. In addition, available alkalinity (about 40%) and extended surface (1800 ft.²/lb.) offer significant advantages for collection and neutralization of acid gases.

For example, a four foot deep lump limestone bed, as suggested for use for HF [13], containing ½ in. diam. spheres would have a surface area of 0.84 ft.²/lb. of limestone. This bed collected up to 96% of HF but required removal of the CaF_2 formed for continued operation at high efficiency. If limestone is assumed to cost $5/ton, then each square foot of reaction surface costs 0.3¢. For slag wool, with a cost of $20/ton, each square foot of reaction surface costs 0.0005 cents per pound. In addition, slag wool will simultaneously remove sub-micron particulate materials with 90 to 99% efficiency, which is not possible with ½ in. granules. Resistance to flow through two in. slag wool filters (with an HF efficiency of 95%) is on the order of one or two in. of water, or if continuously moistened, at most 6 in. of water, which is considerably less than resistance in a packed tower four ft. deep. Cost comparisons on the basis of surface area for many typical tower packings have indicated that small diameter fibers are relatively inexpensive [13]. Advantages of simultaneous removal of three major classes of contaminant are also present in fine fiber filters.

Acknowledgements

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The Deterioration of Materials in Polluted Atmospheres*

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There are a number of undesirable effects of air pollution which are well recognized by those of us who have spent considerable time in densely populated areas. Some of the more obvious of these effects might be listed as follows:

(1) Annoyance to the senses
(2) Impairment of visibility and sky darkening
(3) Impairment to health of humans and animals
(4) Dark or light soiling
(5) Damage to vegetation
(6) Damage to materials

Most discussions of air pollution effects tend to emphasize any one of the first four of these effects because they are the usual manifestations which are most closely associated with our personal lives. Yet, the deterioration of non-living materials resulting from atmospheric pollution is a significant drain on the economy of any heavily populated and industrial area. Although truly valid cost data are still not available, as early as 1930 it was estimated that yearly damage to building property alone in England cost in excess of two million pounds.[1] Much of this type of deterioration goes relatively unnoticed because it cannot always be distinguished from what might be called *normal* or *natural* deterioration.

The atmosphere which surrounds the earth is several hundred miles deep, but even so can be considered only the skin on the orange which is our globe. The thickness of the atmosphere which concerns us in air pollution problems is smaller by several orders of magnitude and can vary between a few thousand and a few hundred feet above ground, depending upon the dispersing properties of the atmosphere.

Our atmosphere is mostly nitrogen with about 20% oxygen, about 0.03% CO_2, and the rare gases (A, Ne, Kr, He) and hydrogen making up less than 0.1%. The more abundant of these so-called rare gases exist in amounts which are several orders of magnitude greater than the concentration of some air pollutants which even at these infinitesimal levels can have devastating effects upon materials.

It has perhaps been implied that the only air pollutants which can affect materials are gases. This is not the case. In general, air pollutants can exist in any of the following physical forms:

(1) Solids
  a) Large dust
  b) Microscopic dust
(2) Liquids
  a) Large droplets
  b) Microscopic droplets
(3) Gases

As with any of air pollution's undesirable effects, the deterioration of various materials is not necessarily associated with any single one of these physical forms. Interactions between physical forms, as well as atmospheric chemical reactions, have been found to be astonishingly complex.

Weather Effects

The bulk of this lecture will deal with the effect of fairly specific atmospheric pollutants on a number of materials, but there is a need to understand some of the physical factors which bring about the build-up of pollutants in the atmosphere and cause them to come in contact and react with these materials. The atmosphere which bathes us is continually in motion, but the character of this motion varies over a wide range. The simplest types of air pollution situations involve single point sources emitting single pollutants that cause deterioration of materials in the immediate surroundings. In such cases the pollutants producing the effect usually have not undergone any appreciable physical or chemical change between the time of their release and their contact with the affected materials. Therefore, it is usually possible to establish the cause and effect relationship by means of measurements of single pollutant concentrations as they relate to wind direction and velocity. In fact, given a point source of pollutant represented by a tall smoke stack free from obstruction, such as buildings, and located in level terrain, it is possible to predict (with various degrees of accuracy) the concentration at any point downwind of the stack under a variety of conditions of turbulence. Since such localized situations as these are fairly easy to recognize and only one

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source is involved, the means for correction should be straightforward.

It is the area-wide effects of air pollution from a multitude of sources of various kinds which require detailed study and are the justification for regional air pollution control agencies. In this type of situation the cause and effect relationship is not easy to establish.

Topography and the Temperature Inversion

Most heavily populated areas in hilly terrain are located in valleys because of the availability of waterways and other transportation arteries. From an air pollution standpoint this is undesirable because during periods of little wind movement pollutants tend to build up within these valleys.

These periods of low wind speeds are often associated with an atmospheric condition known as the temperature inversion which means that the temperature structure has become *inverted* from the so-called *normal* condition. To illustrate, if one were to measure temperatures vertically above ground over a level field somewhere in the Midwest on a bright sunny afternoon in late summer he would find that temperature would probably decrease in a fairly regular manner with height. In the example, this would be considered a *normal* condition. Along the West Coast, on this same afternoon say, in Los Angeles or Oakland, one might very well find that the temperature structure above ground would be quite different from this *normal* condition. Starting at ground level the temperature might initially decrease with height to a point several hundred feet above ground, then suddenly the temperature would begin increasing with height to some altitude. This would be called the inversion layer whose thickness and height above ground can vary considerably. Under this simple *normal* condition a puff of smoke or other pollutant would tend to rise and disperse continually because of the presence of turbulence and mixing in the normal air layer. In the *inversion* situation the pollutant would disperse until it reached the bottom part of the inversion layer where further dispersion would be prevented because of the lack of mixing or turbulent currents in the inversion layer. The inversion along the Pacific Coast is associated with the over-all weather conditions in this area and for hundreds of miles to sea and persists through the late summer and fall.

In most areas inversions are observed frequently in the morning following clear nights. They are called radiation inversions. This terminology is used to describe the conditions which occur after the sun goes down and the ground begins to lose heat, thereby cooling the layer of air close to the ground. This layer of cooler air deepens through the night from continued radiation and produces the inverted temperature profile. On the floor of a valley the deepening of the inversion is accelerated because of cool air draining off of the hills into the valley. Any pollutants emitted within this inversion layer tend to stratify without dispersing upward because of the poor mixing conditions. In addition, without the warmth of the sun, the ground and exposed objects tend to become cooler than the surrounding air, and often their surface temperatures decrease to below the dew point. The resulting condensed surface moisture on materials in the presence of corrosive pollutants, whose concentrations are increasing under the stable influence of the temperature inversion, provide an ideal environment for the promotion of certain types of damage to materials.

Atmospheric Pollutants and their Effects on Materials

In surveying the literature on atmospheric corrosion to metals,[2,3] most of the data presented showed the rate of corrosion associated with the general types of atmospheres such as marine, rural, industrial, etc. Industrial categories imply the presence of a mixture of several atmospheric contaminants, but data were difficult to find in the corrosion literature on the exact chemical composition of these industrial atmospheres and the specific mechanism of attack. The emphasis of this paper is on the air pollutants; therefore the remainder of this discussion will deal with a group of fairly specific air pollutants known to produce deterioration of materials, will list the principal sources of these pollutants, and will discuss the most likely mechanisms by which deterioration of a variety of materials can occur.

Carbon Dioxide

This gas is usually not considered an air pollutant since it is a necessary ingredient of even the purest atmosphere for the building of plant tissues in the process of photosynthesis. Although the CO_2 content of the atmosphere is controlled by absorption in the oceans, rain, and by uptake in vegetation, concentrations of this material over heavily industrialized areas, where large amounts of fossil fuels are being consumed, can reach many times the so-called normal value of 0.03%.

Its principal undesirable effect can be found in the deterioration of building stones, and in particular such carbonate rock as limestone.[4] In the presence of moisture the resulting carbonic acid attacks calcium carbonate converting it to the water soluble bicarbonate which is then leached away. It is doubtful that this type of deterioration would occur, as is the case with many other instances of atmospheric deterioration or corrosion, if it were not for the presence of moisture.

Sulfur Dioxide and Sulfur Trioxide

Sulfur dioxide has its principal sources in combustion processes where fuels such as coal and oil containing appreciable amounts of sulfur (1 to 5%) are burned. From sources of this type in New York City it has been estimated that over 1.5 million tons of SO_2 are emitted per year.[5]

Other important sources of SO_2 are in the roasting of sulfide ores and refinery operations where sludges and waste gases high in sulfur are burned. Concentrations of this pollutant sometimes reach several ppm. (parts per million) over short periods of time in areas immediately surrounding such large sources, but over extended periods in areas where there are many smaller sources of SO_2 the concentrations usually average less than 1 ppm. Even at these seemingly low levels, SO_2 is capable of damaging a wide variety of materials. As early as 1939 Burdick and Barkley[6] of the United States Bureau of Mines surveyed the available literature covering the deterioration of many materials in atmospheres containing SO_2. Much of the work was carried out in laboratories under conditions of concentration and pressure which would not normally exist in the free atmosphere, but nevertheless a wide variety of materials were shown to be affected.

Sulfur trioxide is likely to be formed whenever SO_2 is formed in a process, but in much lesser

amounts.[7] Because of its extremely hygroscopic nature it invariably exists in the atmosphere in droplets of sulfuric acid. SO_2 in the presence of sunlight is capable of undergoing auto-oxidation to SO_3 in the atmosphere. The rate for this reaction is low (0.1 to 0.2%/hr.) if the air contains no other contaminants, but there is increasing evidence that the presence of certain constituents in particulate matter such as are found in most polluted atmospheres greatly increases this reaction rate. Further reactions of the acid with other air pollutants appear to result in the formation of sulfates.

Metals

Although aluminum appears to resist attack by sulfur dioxide,[8] many other metals (particularly iron and steel) are strongly susceptible to attack. Those metals which are attacked by SO_2 and SO_3 require the presence of water in vapor or liquid form for the attack to occur. The rate at which iron rusts is greatly accelerated by traces of SO_2 in the air. However, in bone dry air SO_2 has little or no effect on iron and many other metals. It appears that the combination of moisture, SO_2, and particulate matter combine to promote attack on iron. In some work carried out at the Chemical Research Laboratory in Teddington, England,[1] it was shown rusting in a moist atmosphere containing SO_2 is greatly accelerated by the presence of particulate matter. In one experiment, a sample of iron was exposed to a moist atmosphere containing traces of SO_2. Another sample was exposed to the same atmosphere, but protected from particulate matter by means of a muslin cage which permitted only the gaseous constituents to contact the sample. The rusting of the protected sample was negligible compared with the sample which was unprotected. It was not known how much of the moisture and SO_2 were adsorbed by the fabric making up the cage, or whether equilibrium was established.

Sulfur oxides enter into the formation of the well known greenish coating on copper and copper alloys in industrial areas. This consists of basic copper sulfate,[9] but it is extremely resistant to further atmospheric attack and therefore acts as a protective film. However desirable this effect may be from the standpoint of esthetics and further attack, these same reaction products are unwanted when they form on electrical contacts made of copper, thereby changing the electrical resistance of the contacts.

Building Materials

SO_2 is capable of attacking a wide variety of building materials, including limestone, marble, roofing slate, and mortar. Any carbonate-containing stone is damaged by having the carbonate converted to relatively soluble sulfates, and of being leached away by rain water. Other types of stones, such as granite and certain sandstones, in which the grains are cemented together with materials containing no carbonate, are relatively unaffected by SO_2 in the atmosphere.[10]

Leather

SO_2 has a strong affinity for leather. This pollutant causes leather to lose much of its strength and ultimately to disintegrate. As early as 1843 Faraday came to the conclusion that the rotting of leather upholstery on chairs in a London club was the direct result of sulfur compounds in the air.[11]

The storage of valuable leather bound books in city libraries can pose a serious problem. The bindings of books stored in rooms with a free exchange of polluted air were found to deteriorate much more rapidly than those stored in confined spaces or inside of glass cases.

Leather safety belts exposed to polluted atmospheres containing SO_2 can be dangerously weakened in a few years exposure. The analyses of leather which has rotted under these conditions show sulfuric acid contents as high as 6 to 7%.

Paper

In Burdick and Barkeley's Review[6] a report of the work of one research[12] showed that SO_2 in concentrations of 2 to 9 ppm. for a 10 day exposure resulted in embrittlement and a decrease in folding resistance of both book and writing papers.

Textiles

In many areas the average person thinks of air pollution in terms of the dirtying of textiles, yet sulfur oxides alone are capable of causing deterioration to a variety of natural as well as synthetic fibers used in textiles.

Cotton, being a cellulosic fiber like paper is weakened by the presence of SO_2. The work of Race[13] in England as reported by Greathouse[4] showed that the breaking strength of cotton fabric in winter was considerably less than that found in summer. Without the presence of atmospheric pollutants one would expect the reverse to be the case because of the higher sunlight intensity in summer which in itself can cause deterioration of the fabric.

Wool, being a proteinaceous material, behaves similarly to leather and is capable of absorbing and being weakened by SO_2.

Damage to women's nylon hose by air pollution (presumably SO_2 or SO_3) has made newspaper headlines on numerous occasions in many areas. The exact mechanism of the attack has not yet been thoroughly investigated and reported, but it has been shown that a 3% solution of sulfuric acid is capable of reducing the strength of nylon (a polymeric amide) yarn by about 20%.[14] It has been postulated that extremely small atmospheric particles containing adsorbed SO_2[15], or tiny droplets of sulfuric acid which have formed around particles[5] become attached to the very thin nylon fibers and, being under some tension, they fail. Other materials of nylon, such as the fabric in shirts and dresses, are made from fibers of much larger diameter than those of nylon hose and are not under the tension, and are apparently not as noticeably susceptible to this kind of damage.

Hydrogen Sulfide

This highly odorous gas is often associated with the malodor of rotten eggs. There is some question of its odor threshold, but it is probably below 1 ppm.

One of its principal sources has been refinery operations where *sour* crude oil is processed; however, the sulfur can be recovered from this gas in a process that in some instances may ultimately pay for itself. Therefore, H_2S from this source is on the decrease.

H_2S is also released from bodies of water into which substantial amounts of inadequately treated sewage have been dumped. Because of the oxygen deficient environment, the normal sulfate content of these waters is reduced to sulfide which can be released as H_2S. Another

source of H_2S is in the manufacture of coke from coal containing appreciable sulfur.

Hydrogen sulfide can be oxidized in the atmosphere to SO_2 and SO_3, particularly under conditions of high humidity and to some extent its responsibility in atmospheric deterioration can be related to the preceding section on sulfur oxides. However, there are several forms of deterioration which are related directly to hydrogen sulfide gas.

Paint

House paint containing lead compounds is rapidly darkened in the presence of even low concentrations of H_2S by the formation of black lead sulfide. The work of Hess[16] as reported by Greathouse[4] points out, however, that the dark lead sulfide is rapidly oxidized to lead sulfate, thus turning the paint film white. It has been observed in Detroit that pigments in a lead base paint exposed to moist H_2S may show a different color, such as pink or tan.

Since highly polluted atmospheres often contain appreciable quantities of dark particulate matter there is the chance that the dirtying of a painted surface by this kind of material can be mistaken for lead sulfide darkening.

Another type of paint surface darkening which has been confused with hydrogen sulfide damage is caused by certain types of fungi.[17] This kind of damage occurs most frequently where the humidity remains above 60%. It is likely to occur on paints containing a high percentage of raw linseed oil and some of the newer latex emulsion based exterior paints.

Metals

In the presence of H_2S, such metals as silver and copper tarnish rapidly. The sulfide coating formed on copper and silver electrical contacts when separated can increase greatly the resistance across these contacts when they are closed. This may also result in welding the contacts.

Hydrogen Fluoride

This extremely dangerous and corrosive gas is evolved from a variety of processes which include the following:

The production of synthetic fertilizer starting with the acidulation of phosphate rock which invariably contains combined fluorides.

The manufacture of enamel frits and high fluoride glass.

The production of basic aluminum which uses cryolite and other fluorine compounds in the electrolytic reaction.

The production of steel where the ore contains fluorides and where fluorspar is used as a flux.

Being a corrosive gas and at the same time extremely hygroscopic, it can attack a wide variety of metals and glass, or enamel-coated materials.

There is at least one report in the literature[18] of HF attacking window glass to the extent that the glass was rendered opaque. This effect has been noted by the author on several occasions. It should be pointed out, however, that the concentrations required to produce visible damage to glass and other materials are felt to be far in excess of those required to kill many types of vegetation. Certain types of plants such as gladiolus are extremely sensitive to HF and are damaged by concentrations in the ppb. dilution range. In addition, cattle feeding on vegetation exposed to relatively low concentrations of HF are subject to fluorosis. Therefore, other than occasional localized damage, hydrogen fluoride does not appear to be an important contributor to the deterioration of materials simply because it cannot be tolerated for other and more urgent reasons.

Ozone and Photochemical Smog

Ozone has been measured at various points over the world, and concentrations at ground level in most areas appear to be in the range between 0 and 5 parts per hundred million (pphm). Within the stratosphere the concentrations may be as high as 600 to 800 pphm. However, it is not likely that the low natural levels of ozone near the ground result from diffusion downward from the stratosphere. The natural ozone concentrations at ground level are more likely to be formed by the action of sunlight. Regardless of this, ozone levels in certain polluted atmospheres such as those found under so-called *smog* conditions in the Los Angeles area and, to a somewhat lesser degree, in the San Francisco Bay Area, can rise to concentrations many times those associated with normal *background* levels.

The relatively high ozone levels are related to a series of complex chemical reactions occurring in the atmosphere[19], many of which are now understood, but many of which are still being learned about. Haagen-Smit[20,21] and his co-workers carried out the first experiments which showed that low concentrations of hydrocarbons in the presence of nitrogen oxides and sunlight produced unusually high ozone levels. Without sunlight the ozone levels drop back to the *normal* range. More recent work at the Franklin Institute[22] has contributed considerable insight into the nature of these reactions but, at the same time, has confirmed earlier observations that the chemistry of polluted atmospheres is fantastically complex.

The principal sources of photoreactive hydrocarbons and other organic vapors in the atmosphere are the exhausts from automobiles and other internal combustion engines, refinery operations, solvent losses from a variety of operations, and inadequate incineration. Oxides of nitrogen are part of the normal effluents from any high temperature combustion operation in which air is the source of oxygen, since some of the nitrogen is oxidized.

The high ozone level during some smog conditions is but one of the undesirable manifestations; others include eye irritation, reduced visibility from the formation of aerosols, and vegetation damage. However, the high ozone content or oxidizing capacity of atmospheres polluted in this manner is largely responsible for most of the observed serious deterioration to materials associated with this type of smog.

Rubber and Elastomers

One of the early indications of the smog problem in Los Angeles was the excessive cracking of rubber products. It had long been known that atmospheric oxygen and especially ozone could cause rubber cracking. Crabtree and Kemp[23,24] carried out extensive studies as early as 1946 on the attack of natural rubber by light-energized oxygen and ozone. The cracking of rubber in an ozone atmosphere of even high (1 to 5%) concentrations does not appear to proceed until the rubber is stretched. Even the slightest stretching under these conditions brings about rapid

deterioration. The Los Angeles Air Pollution Control District uses as one of its measurements of ozone concentration in the atmosphere a method developed by Bradley and Haagen-Smit[25] in which bent strips of rubber of precise formulation are exposed to the air to be sampled. By determining the depths of cracks at the end of definite exposures it is possible to estimate the ozone content of the atmosphere.

According to present theory, elastomers of the unsaturated type are attacked by ozone at the double bond in the carbon-to-carbon chain.[26] If the chain is under stress, it breaks, which leaves its neighbor under additional strain. Synthetic rubbers such as butadiene-styrene, or butadiene-acrylonitrile, being unsaturated, are affected in this same manner. Neoprene, although unsaturated, resists ozone attack, presumably because of the presence of the chlorine atom adjacent to the double bond. Butyl, thiokol and silicone polymers, being saturated, are highly resistant to attack by ozone.

The literature references on the subject of deterioration of rubber in ozone-containing atmospheres testify to the seriousness of this kind of damage. This effect is especially important to tires and insulated utility wires.

Textiles and Dyes

Ozone has long been known to affect the strength of fabrics and the color fastness of dyes.[27,28,29,30] Only recently, however, have any experiments been carried out to determine the quantitative effects of ozone as related to community air pollution mixtures on fabrics and dyes. Some recent research by a committee of the American Association of Textile Chemists and Colorists[31] presented preliminary results on the exposure of a group of different fabrics and dyes to Los Angeles smog. The samples were exposed in chambers which provided free passage of contaminated air inside the chamber, but permitted no direct sunlight to strike any of the samples. Because this was a preliminary investigation, no conclusions were drawn other than the statement that exposure to smog conditions did cause definite deterioration of a number of fabrics and dyes.

It is certain that this type of smog is detrimental to a number of natural and synthetic materials, but the awareness to and understanding of the many factors are so new that active research projects on several of the factors are just now getting underway.

Solid Particulates and other Damaging Agents

The role of solid air pollutants in causing deterioration is normally thought to be that of soiling. This can be either the soiling of light surfaces such as a table cloth, or white marble column on a building, with dark-colored particulate matter such as soot; or the soiling of a dark surface, like a polished mahogany table by light colored solids such as cement dust. The soiling does not necessarily cause deterioration directly, but its removal does. Much money has been spent in cities where large quantities of coal are burned to sandblast off the sooty layers which have accumulated on prominent buildings. One aspect of this effect stressed by Greenburg and Jacobs[5] is somewhat unique; the tarry components of carbonaceous material resulting from poor combustion of coal or oil are likely to be sticky and also acidic in nature. Therefore, the corrosiveness of solid particles on which they would adhere are likely to persist over extended periods of time when they are not flushed off by rain.

The direct or chemical deterioration of materials as a result of solid particulates collecting upon their surfaces depends upon the chemical activity of the solid in its environment and the susceptibility of the receiving material.

Preston[32] *inoculated* various metallic surfaces (coated and uncoated) with fine powders or *nuclei*. He used such materials as sodium chloride, ammonium sulfate and chloride, sodium nitrate and flue dust. The samples were then exposed to atmospheres held at various humidities and the resulting corrosion was measured. The character of the corrosion was the typical filiform corrosion common to the corrosion observed from many highly reactive particulates in the atmosphere. In most of the cases in this study corrosion increased with humidity. One exception was ammonium chloride; however, the addition of traces of SO_2, to the test atmosphere greatly increased the corrosion at high humidities. It should be pointed out that these experiments were carried out in a laboratory environment, and did not duplicate actual outdoor conditions.

A more specific occurrence of damage to materials from atmospheric solids resulted from the deposit of iron particles from a grinding operation on parked automobiles.[33] It was noted that brown particles were attaching themselves tenaciously to the paint of automobiles in a parking lot. A brown stain surrounded each particle and many cars had to be repainted. The particles at the center of each stain were identified microscopically as iron grindings or cuttings based largely on their peculiar shape. The mechanism of the staining was felt to be more complex than simple rusting. The authors postulated that it resulted from the formation of ferrous hydroxide in the presence of moisture which, being in a colloidal form, diffused into the paint film, and upon drying and oxidizing left the brown stain of ferric oxide.

While discussing damage to automobile finishes it should be pointed out that the automobile is an excellent indicator of corrosive or damaging atmospheres because the owner always has extreme pride and large investment in ownership, and most instances of damage are quickly brought to the attention of those in charge of air pollution control programs. In Detroit[34] the air pollution control agency accumulated numerous records of various kinds of damage to automobile finishes.

The same type of damage from iron particles as mentioned above was experienced in Detroit; however, it was theorized there that in the presence of moisture some of the oxygen for the formation of iron oxide came from the paint itself. The result was a pit, filled and over-covered with a bump of iron oxide.

Cars parked near demolition operations where brick buildings were being taken down were severely damaged by mortar dust in the presence of moisture. The damage could be reproduced by sprinkling mortar dust on paint test panels and covering with a moist blotter. The damage had the appearance of crazing. No attempt was made to identify the damaging agents in the dust.

Other damage to auto finishes in Detroit was by chromic acid mist, which formed a brown stain on light-colored cars, and a *blush* on the darker shades of paint. Repainting was required because the color change

could not be removed by washing or polishing.

Sodium carbonate particles from such operations as soda ash manufacture, or as a breakdown product from cyanide heat-treat bath evaporation created a characteristic pit in the paint surface. Each pit contained a white particle and the pits were thus easily identifiable on dark paint surfaces. The white specks could be removed by washing, but of course the damaging pit remained.

Conclusions

The deterioration of materials resulting from atmospheric pollution is a serious economic loss. Beyond this, it is related to a number of complex atmospheric and surface reactions, all of which could use further study. The atmospheric corrosion engineers and specialists who must investigate deterioration of materials need to familiarize themselves thoroughly with the physical environment in which they carry out their measurements. This knowledge of the environment includes not only the physical factors which influence the form and manner in which the agent contacts the materials, but perhaps more important knowledge of the chemistry of the specific agents which singly (or in combination) lead to the ultimate damage to materials.

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System Designs for the Catalytic Decomposition of Nitrogen Oxides*

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During the past decade, since the Catalytic Combustion Process was first introduced for the control of air pollution, thousands of installations have been placed in service. In this short time, the reliability of catalysts to serve as an effective tool in the oxidation of hydrocarbon and organic type vapors has been given wide recognition. In contrast, much less is known regarding the ability to utilize catalytic principles for the reduction — or deoxidation — of other types of atmospheric contamination. Consequently, this paper presents theories on the catalytic destruction of nitrogen oxides, describes system designs currently in use on industrial applications, and gives available data on operating performance.

Investigations by various authorities indicate that the oxides of nitrogen play an important role in the formation of smog [1]. It is therefore to be expected that future air pollution control standards will require the same vigilance toward elimination of nitrogen oxides as now exists in the removal of hydrocarbon, aldehyde, and various sulphur bearing gases. Accordingly, this discussion will be confined to control of exhausts from industrial and chemical operations containing harmful concentrations of these oxides. Even in localities where the smog-forming aspect is of secondary interest, reduced emission of nitrogen oxides may be necessary, or desirable. Reduction to concentrations below toxic levels before discharge to the atmosphere provides protection to in-plant and nearby personnel. Protection of adjacent structures and equipment from the corrosive effects of nitric acid formation may dictate the need for corrective action.

A prominent source of nitrogen oxides is to be found in the waste gas emissions from nitric acid production. Other industrial operations using organic nitrogen compounds and acid-reacting processes are among those for which Catalytic Combustion systems have been successfully employed. Concentrations of nitrogen oxides in these waste gases range from less than 0.1% to almost 50% by vol. Included are NO, NO_2 nitric acid vapors, and their polymers.

This paper will include flow arrangements for systems operating at atmospheric as well as elevated pressures, along with their relation to plant operations. Discussion of the principles by which catalytic reduction is accomplished will be presented, and factors required for satisfactory system desgins will be outlined.

While it is recognized that oxides of nitrogen are present in small concentrations in the exhausts of internal combustion engines, boilers, and various fuel fired equipment, the application of catalysis for their correction wil not be considered here.

The Catalyst and its Function

A catalyst is a promoter, or accelerator, of chemical reactions. While aiding a reaction, it does not itself enter into the end products, nor is it permanently affected by the chemical changes which occur. In the oxidation of hydrocarbons, for instance, it causes oxygen to be combined with the fuel in the same chemical reaction as when using a burner to product flame combustion. An important difference is that the catalyst promotes the reaction with fuel concentrations below the flammable range, and without need for control of the fuel-air ratio. Complete catalytic oxidation of hydrocarbons proceeds to carbon dioxide and water vapor, as in the simplified equation

$$(n_1)\mathrm{HC} + (n_2)0_2 = (n_3)\mathrm{CO_2} + (n_4)\mathrm{H_20}$$

Thus, the reaction renders the effluent free of contamination, odor, and visible plume. Platinum type catalysts are widely recognized for their ability to permit this reaction to proceed at low temperatures — in the range of 450 to 600°F. for most hydrocarbons.

Efforts at decomposition or removal of nitrogen oxides, as a means of air pollution control, have included absorption, adsorption, and the application of heat alone in the presence of a catalyst. The former methods require subsequent desorption, or secondary disposal of the collection media, as well as large collection capacity for continuous industrial processes [2]. The latter method has shown a measure of success at very high temperatures, but efficiencies are low, and the method appears to be impractical at prevailing fuel costs in most areas [3]. Recently, however, it has been found that the use of a catalyst can complete the decomposition desired, when nominal amounts of fuel are added to promote the reaction.

By mixing a hydrocarbon, or re-

*Presented at the 51st Annual Meeting of the Air Pollution Control Association held at Philadelphia, Pa., May 25-29, 1958.

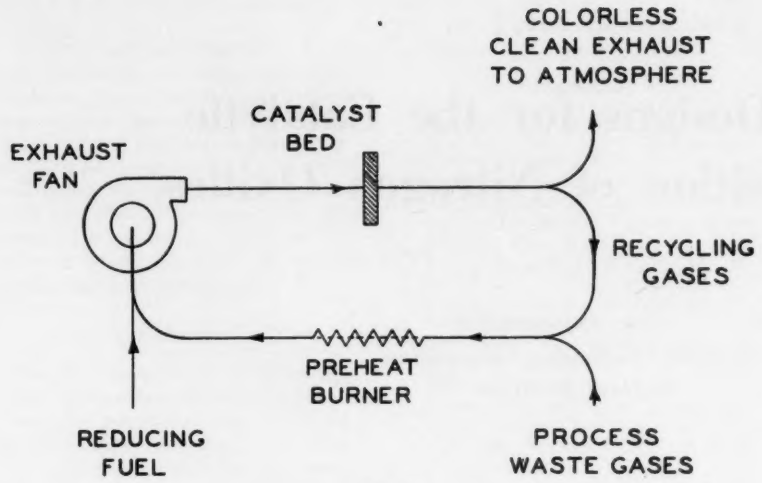

Fig. 1

active fuel with the gases, and passing them through a catalyst, the equation

$$(n_1)NO_x + (n_2)HC = (n_3)H_2O + (n_4)CO_2 + (n_5)N_2$$

can be made to proceed to completion at comparatively low temperature. Consequently, it can be seen from the equation that the end products are again odorless, color-free, and harmless gases. The amount of free oxygen contained in the fume stream presumably influences the ease with which the reaction can be completed. Obviously, when the fume stream is entirely devoid of free oxygen, then oxidation of the hydrocarbons can occur only through simultaneous reduction of the nitrogen oxides to free nitrogen. Nevertheless, complete removal of the characteristic color and odor can be accomplished with free oxygen concentrations approaching that of air [4].

Functions of System

Long term operations on hydorcarbon gases have shown that catalysts will function reliably when proper conditions are maintained. These conditions have been covered in detail in earlier papers [5], but a review of the essential factors contributing to successful performance may be helpful:

(1) The system must have sufficient capacity, in terms of active catalyst surface, for the design flow rate and reactant concentration.

(2) The stream entering the catalyst bed must be maintained above the minimum catalyst ignition temperature required for the particular reactant.

(3) Uniform velocity distribution of the stream entering the catalyst bed is required to assure maximum utilization of the available catalyst surface.

(4) Uniform temperature distribution is required to permit operating the catalyst at the lowest practical temperatures.

(5) Thorough mixing of the reactant with the fume stream is required to assure availability of the fuel throughout the catalyst bed.

Most Common Fuels Can Be Used

As shown above, a reactant fuel must be introduced into the system for the decomposition reaction to take place on the catalyst. Most of the commercially available gases can be used. Often, inexpensive by-product gases are available from other processes, and might contain methane or other saturates, hydrogen, or carbon monoxide. With proper design considerations, some liquid fuels may be employed. The selection of the type of reactant fuel determines the required operating temperature range of the catalytic system. This is due to the fact that various hydrocarbon fuels have different minimum catalyst ignition temperatures. [5] This property may, or may not, be influenced by the presence of nitrogen oxides, or the fuel concentration required. Likewise, the heat release of the combustible on the catalyst might be influenced by the fixed nitrogen compounds.

Common nomenclature denotes the fuel metered into a system for reaction on the catalyst as the "sparge" fuel, as contrasted to preheat or burner fuel.

Catalytic reduction of nitrogen oxides can be accomplished at either atmospheric or elevated pressure. In some chemical processes, such as the modern nitric acid plant, economic advantages are gained in treatment of the gases before expansion. In others, the oxides are generated and reduced at atmospheric pressure. While each proposed installation requires individual engineering considerations, the designs can be broadly classified as either atmospheric, or pressure systems.

Atmospheric Pressure Systems

For operations at atmospheric pressure, system designs which had previously been developed for hydrocarbon oxidation are being employed, with modifications, to control the condition of the exhaust. The "R-C" or recycling system is a typical example.

The flow diagram in Fig. 1 illustrates the operation of the system. The main components are the preheater, exhaust fan, and catalyst bed. As the process waste gases enter the system, they become mixed with and preheated by the recycled portion of the stream. The combined stream then passes the preheater, usually a conventional premix type gas burner, where the remaining heat requirement is satisfied. Following this, the reducing fuel is sparged into the system, and the combined stream enters the exhaust fan, is thoroughly mixed, and discharged through the catalyst element. Here, the oxidation of the sparge fuel and reduction of the nitrogen oxides takes place, with heat release in proportion to the sparge fuel supplied. The temperature rise through the catalyst bed may exceed 500°F., or more, depending on the concentration of nitrogen oxides which must be reduced.

A portion of the high-temperature gases leaving the catalyst are then recycled to accomplish the fume preheating and dilution function. The remainder is released to the atmosphere free of the noxious and corrosive oxides. A cut-away view of a typical system design is shown in Fig. 2. The unit is fabricated with heat and corrosion resisting steel inner liner and internal parts. High temperature insulation is applied to the liner and covered by a steel

protecting jacket. The assembled unit is mounted on a structural steel base. Necessary access panels are included for servicing the catalyst bed and inside parts.

The entire system, as described above, is fabricated, shipped, and installed as a fully assembled unit, requiring only final duct, stack, piping, and electrical connections in the field. A fully integrated control system, incorporated in a prewired cabinet, is included.

Design Considerations

The location of components plays an important part in the successful operation of the system. Placement of the fan in the flow pattern between the preheater and the catalyst bed provides the necessary mixing of the process, recycle, and sparge gases with the products of combustion from the preheat burner. In addition, control of the velocity distribution of the mixed gases is maintained over the face of the catalyst bed.

The functions of the recycling feature are the same as for catalytic systems used for the conventional purpose of oxidizing hydrocarbon vapors. (6)

Usually, only normal precautions must be taken to prevent catalyst poisoning or paralyzing agents from entering with the waste gases. Products of upstream corrosion can coat and inactivate the catalyst surfaces; selection of suitable construction materials eleminates this possibility.

Systems for Elevated Pressures

The most common source of nitrogen oxides at high pressure is in the tail gas streams from nitric acid plants. The usual practice has been to pass the waste gases through an expansion turbine, or reciprocating engine, to recover usable power. Upon release from the stack, the gases exhibit the dark reddish-brown plume characteristic of NO_2.

The volume of gas, analysis, and pressure prior to expansion varies with individual plant designs. However, a typical nitric acid plant may have 20,000 cfm., (70°F. and atmospheric pressure equivalent) containing up to 0.5% nitrogen oxides, and available at pressures up to about 100 psig.

Prominent designers of nitric acid plants now incorporate a Catalytic Pressure Reactor, installed between the process tail gas outlet and the expansion turbine. A dual result is thus obtained; the catalyst reduces the oxides of nitrogen to produce a clear, clean, effluent, and the power recovered through the turbine is increased many times by the greatly elevated temperature of the gases — caused by the catalytic reaction with the reducing sparge fuel.

Pressure reactors with turbine outputs exceeding 2000 hp. are now in use, and larger units are under consideration. Where early installations may have been motivated by the need for control of an air pollution problem, this is now frequently of secondary importance to the value of the recovered power. This is further emphasized by increased utilization of the catalytic reactor and turbine arrangement on pressurized systems in the organic and petrochemical fields where tail gases contain no objectionable contamination.

Fig. 3 shows a complete unit, ready to be installed and placed into operation. The plant waste gases enter through the side inlet nozzle, are directed upward around the main shell in an annular area to the top of the vessel. At this point the flow turns downward into a second annulus and enters a hollow cylindrical catalyst bed. The gases than pass inwardly through the catalyst bed into the discharge nozzle, leaving the vessel from the bottom outlet.

The same vessel, with the upper shell removed to reveal the compact cylindrical catalyst cartridge, is shown in Fig. 4.

Specially designed sparging inlets are arranged to produce intimate mixing of the reactant fuel with the waste tail gases before entering the catalyst bed. Temperature control and limit protective circuits are interlocked with related process operations.

Catalyst Structure

Although the hollow cylindrical type catalyst bed is shown, flat bed catalysts are also used. In either case, the catalyst media is of all-metal construction, consisting of high-nickel crimped ribbon supporting metal upon which the precious metal catalyst is electrolytically deposited. The construction is capable of withstanding very high temperatures; several sys-

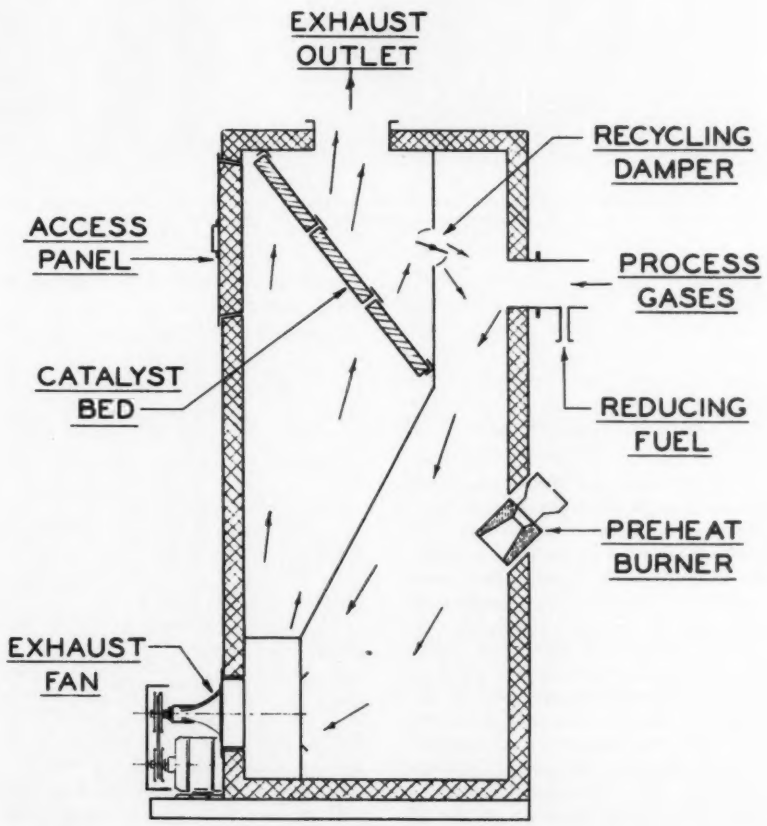

Fig. 2

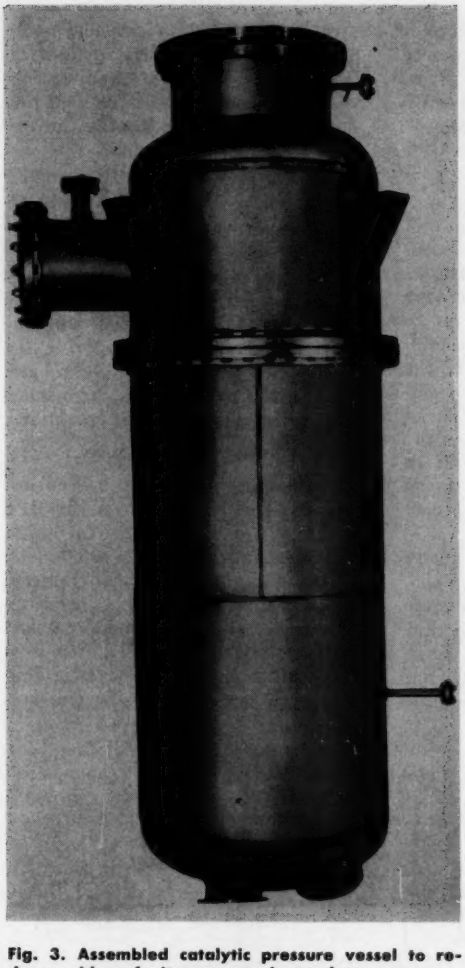

Fig. 3. Assembled catalytic pressure vessel to reduce oxides of nitrogen at elevated pressures.

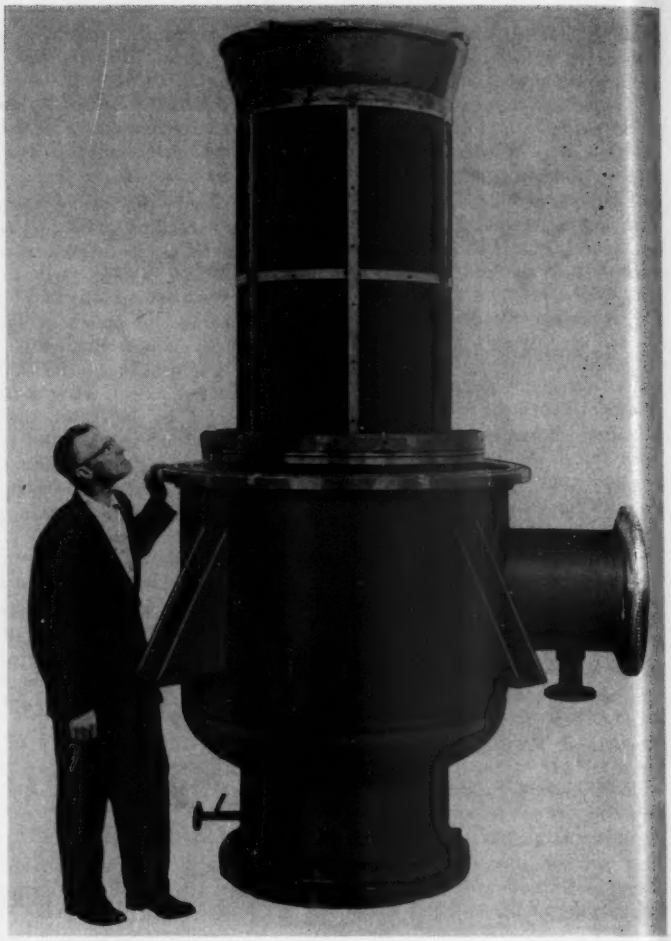

Fig. 4. Catalytic pressure vessel with upper shell remove to show cylindrical catalyst cartridge.

tems are operating above 1600°F. Where applicable, the cylindrical catalyst configuration permits minimum pressure drop for the gases passing through the bed, and at the same time provides the space necessary for the required amount of catalyst surface in a small vessel.

The preheating requirement for the waste gases at high pressure is available from a number of sources. Heat exchangers may be employed, either to extract heat from other plant sources or from the hot exhaust from the catalyst system itself. In the former instance, a waste heat boiler may be employed to reduce the temperature of the stream leaving the catalyst to maintain the required turbine inlet temperature. Indirect fuel-fired preheating equipment is available, but is now being supplanted by direct-fired high pressure gas or oil burners. These may be incorporated in the same vessel as the catalyst, to burn directly in the gas stream.

Operating Temperature Limits

Conventional catalytic systems in use to oxidize combustible contaminants for air pollution control are generally operated at catalyst entry temperatures from about 450 to 600°F., for normal hydrocarbon vapors. The temperature of the discharging gases will range anywhere from very close to the entry temperature, for trace concentrations of the combustible, to 1200°F. or more.

In contrast, systems to reduce the oxides of nitrogen may operate in some cases with entry temperatures close to ambient, or as mentioned, with exhaust temperatures above 1600 °F. A unit whose only function is to decontaminate the effluent will be operated at temperature levels which will produce the required results with the maximum fuel economy. Where heat or power recovery is required, in addition to the prime factor of pollution correction, higher temperatures may be desirable. Often the thermal level will be dictated by the gas temperature leaving the process, the design limitations of recovery equipment, the oxygen concentration, or the reactant fuel used.

Performance

To date, there have been no reports of personnel discomfort, or corrosion, attributed to exhaust streams whose oxides of nitrogen content have been reduced by processing in a catalytic system. In every case, users report complete elimination of the characteristic color and odor, which are otherwise strongly in evidence.

One contention is that the nitrogen oxides must be reduced to less than 300 ppm to effect complete color removal in gases exhausted to atmos-

(Continued on page 222)

Some Factors Affecting the Concentration of Oxides of Nitrogen in Exhaust Gases from Spark Ignition Engines

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It is well established that exhaust gases from internal combustion engines contain small amounts of oxides of nitrogen. Air pollution authorities are concerned with this fact since these compounds are believed partly responsible for the atmospheric pollution found in the Los Angeles area. Although oxides of nitrogen come from many sources, automobiles are reported to be important contributors [1]. On the basis of such reports, air pollution authorities have urged the development of methods and devices to reduce the emission of oxides of nitrogen from automobiles. To provide information relevant to this control problem, the present study was undertaken.

Hanson and Egerton[2], Arnoldi[3], and Spindt, Wolfe, and Stevens [4] have studied the formation of oxides of nitrogen in exhaust gases from internal combustion engines. Hanson and Egerton showed conclusively that oxides of nitrogen are formed in the combustion process, and not only in the spark discharge as had previously been suggested. Arnoldi and Spindt, Wolfe, and Stevens both studied the effects of some engine variables. However, none of these investigators used an engine designed in accordance with modern automotive standards, nor did they study operating variables over as wide a range as is believed desirable for the air pollution problem.

*Presented at the Symposium on Air Pollution, 132nd Meeting of the American Chemical Society, New York, N. Y., Sept. 9-13, 1957.

Experimental

Equipment

The single-cylinder spark ignition engine used in this investigation was patterned after a production passenger car engine. Combustion chamber design was very nearly identical to that of the prototype engine, and many parts, including pistons and valves, were production parts. A schematic drawing of the engine is shown in Fig. 1 along with the associated equipment used to control and measure engine operating variables. Manifold air pressure was regulated by the critical-flow-orifice supply system. Electrical heaters controlled both the carburetor air temperature and the mixture temperature. The carburetor, a single barrel automotive type, was modified so that fuel flow and thus air-fuel ratio could easily be varied. Spark timing was manually set with a conventional distributor. Compression ratio was varied by changing cylinder heads.

A sampling port was tapped into the exhaust line about 12 in. from the engine. The port had two outlets, one connected to an Orsat analyzer and the other used to collect grab samples. Orsat analyses, rather than measured air and fuel flow rates, were used to determine air-fuel ratio.

Procedure

The following engine variables were studied:

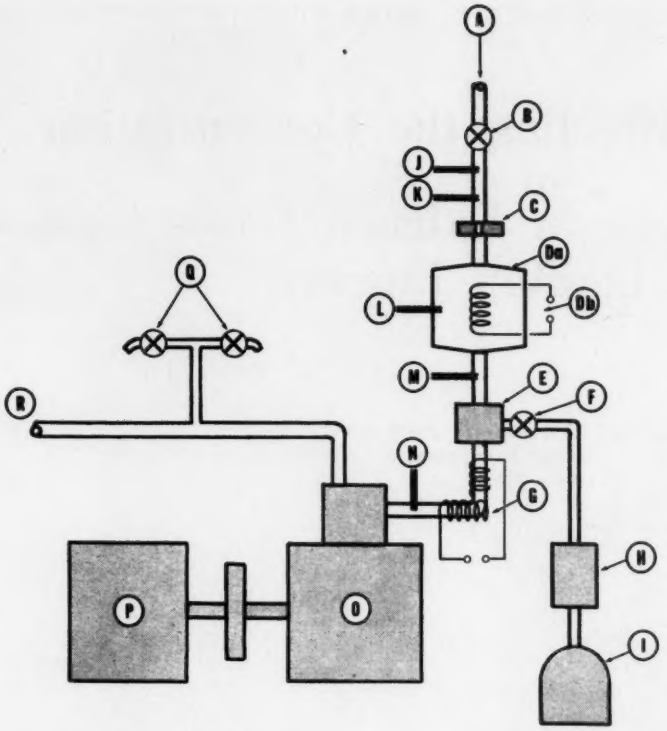
Air-Fuel Ratio
Spark Timing
Manifold Air Pressure
Engine Speed
Compression Ratio

Combinations of these variables used in the investigation are shown in Table I, which also indicates the general design of the experiment. Each "X" in Table I represents a test series in which engine speed, spark timing, and manifold air pressure were fixed as indicated, and the air-fuel ratio varied from 10 to 20. Twenty to thirty individual tests, each at a different air-fuel ratio and each involving three replicate analyses for oxides of nitrogen, made up each test series. Engine operating temperatures are shown in Table II.

For all tests where knock was no problem, commercial grade isooctane was used as fuel. In those few tests requiring a fuel of higher antiknock quality than isooctane, either leaded isooctane (3 cc. TEL/gal.) or triptane was used. Tests at non-knocking conditions showed no significant differences between these three fuels with respect to the concentration of oxides of nitrogen found in the exhaust gases.

Sampling and Analysis Methods

Although nitric oxide is believed formed in the combustion process, other oxides of nitrogen, notably nitrogen dioxide, may be present in exhaust gases due to secondary reactions. Nitric oxide may also react to form other oxides of nitrogen after the gas sample has been col-



(A) High Pressure Air
(B) Pressure Regulator
(C) Critical Flow Orifice
(Da) Surge Tank
(Db) Air Heater
(E) Carburetor
(F) Fuel Control Valve
(G) Mixture Heater
(H) Fuel Pump
(I) Fuel Can
(J) Upstream Air Temp.
(K) Upstream Air Pres
(L) Manifold Air Pressure
(M) Carburetor Air Temperature
(N) Mixture Temperature
(O) Single Cylinder Engine
(P) Dynamometer
(Q) Sampling Ports
(R) Exhaust Line

Fig. 1. Single cylinder engine and associated equipment.

TABLE I

Combinations of Engine Variables Investigated

Compression Ratio	6.7					9.5		12.0
MAP — In. Hg.	10	15	20	29	40	15	29	29
Spark Timing — ° BTC								
0°				X			X	X
15°				X			X	X
30°	X	X	X	X	X	X	X	
45°				X			X	

Each of the combinations, indicated by an X, was tested at 1000 rpm. engine speed. Additional tests were made at 500, 2000, and 3000 rpm. at 6.7 compression ratio, 29 in. Hg. MAP and 30° BTC spark advance.

TABLE II

Engine Operating Temperatures

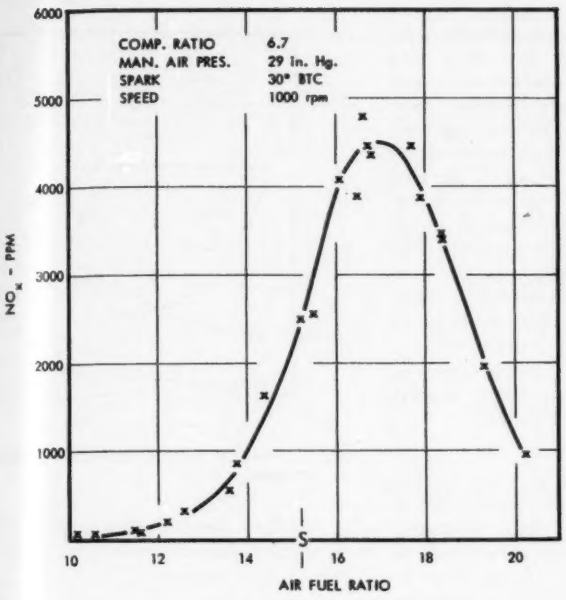
Cooling Water	175 ± 5 °F
Engine Oil	195 ± 5 °F
Fuel-Air Mixture	125 ± 2 °F
Carburetor Air	110 ± 2 °F

lected. Therefore, to determine the total amount of nitric oxide formed in the engine, it is necessary to use a method of analysis which measures the combined amounts of nitric oxide, nitrogen dioxide, and, preferably, higher oxides of nitrogen as well. The phenol disulfonic acid or PDS method [5], which was used in this investigation, meets this requirement. The PDS method measures all oxides of nitrogen, except nitrous oxide, plus any organic nitrogen compounds oxidized to nitrate under the test condition. (Neither nitrous oxide nor organic nitrogen compounds are believed present in exhaust gases.) The PDS method does not identify the individual oxides of nitrogen. Accordingly, results are reported as total oxides of nitrogen and are described in the accompanying graphs as "NO_x."

The exhaust gas samples were collected in calibrated glass bottles of about 500 ml. capacity. Each bottle contained 10 ml. of absorbing solution — 0.1N sulfuric acid plus ten drops of hydrogen peroxide prepared by ten-fold dilution of a 30% solution. This amount of hydrogen peroxide is stoichiometrically equivalent to over 15000 ppm. of nitric oxide. Each bottle was sealed with a three-way stopcock inserted through a rubber stopper and was evacuated to the vapor pressure of the absorbing solution (20 to 25 mm. of mercury) shortly before use.

Gas samples were collected by connecting the side arm of the three-way stopcock to the sampling port with a short piece of rubber tubing, and then manipulating the stopcock to fill and reseal the bottle. Care was taken to purge the connecting line and stopcock. Three consecutive samples were taken within a one minute interval. The pressure in each bottle was measured with an open-end U-tube manometer after the gases had cooled to room temperature, and generally within two hours after the sample was taken. Room temperature and barometric pressure were recorded at the time of pressure measurement.

After overnight standing, the absorbing solution was removed and analyzed for nitrate by the PDS method. Absorption of the oxides of nitrogen and oxidation to nitrate was not materially improved when the standing period was increased to three days. However, absorption was not quantitative in either case. Residual concentrations seemingly independent



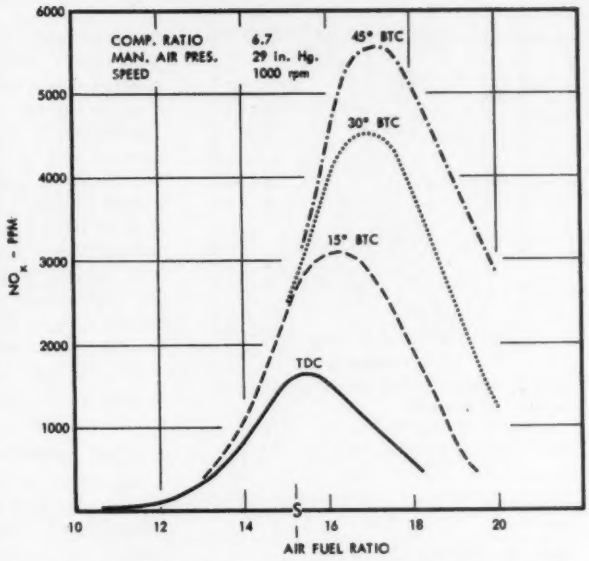


Fig. 2. Effect of air-fuel ratio on oxides of nitrogen (left).
Fig. 3. Effect of spark timing on oxides of nitrogen.

of the initial concentration and averaging about 20 ppm. were found. This small error was not taken into account in reporting the experimental results.

All concentrations of oxides of nitrogen were calculated as ppm. by volume on a dry basis. The size of the gas sample was determined from its pressure, volume, and temperature. Results of triplicate analyses were averaged.

Experiments were made to determine the accuracy and repeatability of the test method. Replicate analyses of a gas mixture containing a known amount of nitric oxide in nitrogen are shown in the second column of Table III. The average of nine analyses was 980 ppm., slightly less than the 1000 ppm. reported by the supplier. The repeatability of the analyses, as judged by the coefficient of variation, was 2.8%.

The last four columns in Table III show replicate analyses of exhaust gases from the single-cylinder engine. Note that the coefficients of variation ranged from 4.3 to 17.7%, considerably greater than with the known gas mixture. This indicates that some of the variability in replicate exhaust gas analyses is due to variations in exhaust gas composition. For example, cyclic variation in engine operation is believed partly responsible.

TABLE III
Accuracy and Repeatability of the Analytical Method

Sample	Measured Concentration of NO_x—PPM. Known Mixture[c] 1000 ppm. NO in N_2	Exhaust Gases from Single-Cylinder Engine at Four Conditions A	B	C	D
1	935	47	263	4380	3500
2	988	43	233	3970	3710
3	954	42	317	3600	3380
4	1000	44	335	3480	3530
5	952	44	393	4250	2590 [b]
6	1018	41	377	3550	3580
7	994	62 [a]	397	3770	3440
8	845 [a]	40	296	3880	3540
9	983	39	369	287 [b]	3390
10	998	43	356	4130	3360
Average	980	43	334	3890	3460
Standard Dev.	27	2.4	59	319	149
Coefficient of Variation	2.8%	17.7%	8.2%	8.2%	4.3%

a Observation rejected by Chauvenet's criterion for reliable data.
b Results rejected—sampling bottle inadvertently opened to atmosphere.
c Blended by the Matheson Company.

Results

Air-Fuel Ratio

A characteristic relationship between air-fuel ratio and the concentration of oxides of nitrogen was observed throughout the tests. An example of this relationship is shown in Fig. 2. It should be noted that the highest concentrations were formed when the air-fuel ratio was somewhat leaner than stoichiometric, and that the variation between the highest and lowest concentration was about one hundred fold.

Because the concentration of oxides of nitrogen is extremely dependent on air-fuel ratio, the effects of other engine variables cannot be interpreted correctly unless comparisons are made at nearly identical air-fuel ratios. Inasmuch as the effect of these other engine variables may

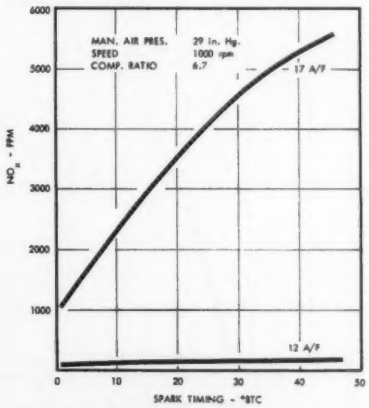


Fig. 4. Spark timing cross-plot.

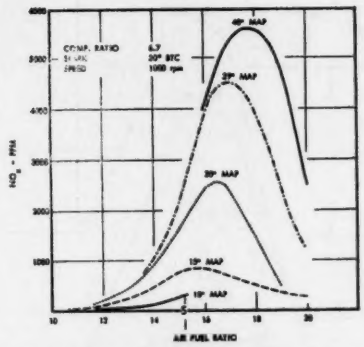


Fig. 5. Effect of manifold air pressure on oxides of nitrogen.

change with air-fuel ratio, all data in the following sections will be presented on NO_x — A/F plots with the variable under study as a parameter.

Spark Timing

The effect of spark timing on the concentration of oxides of nitrogen depended on air-fuel ratio. A family of curves illustrating this effect is shown in Fig. 3. With lean mixtures, advancing the spark resulted in large increases in the concentration of oxides of nitrogen, whereas with rich mixtures spark timing had little or no effect. These same data are cross-plotted in Fig. 4 at one lean and one rich air-fuel ratio to emphasize this dependency on air-fuel ratio. It is interesting to note that the concentration of oxides of nitrogen continued to increase as the spark was advanced beyond the maximum power setting, about 27° BTC for the engine conditions shown in Fig. 3.

Tests at other compression ratios showed essentially the same effect of spark timing.

Manifold Air Pressure

The concentration of oxides of nitrogen increased with increasing manifold air pressure (MAP). As with spark timing, the effect was greatest when the air-fuel ratio was one to three ratios leaner than stoichiometric and became less important at rich air-fuel ratios. Data are shown in Figs. 5 and 6. The five curves in Fig. 5 correspond to operation at 10, 15, 20, 29, and 40 in. of mercury manifold air pressure. The first four of these very nearly cover the load range encountered in automotive service. Operation at 40 in. of mercury simulates supercharging.

Limited tests showed the effects of manifold air pressure to be similar at other compression ratios.

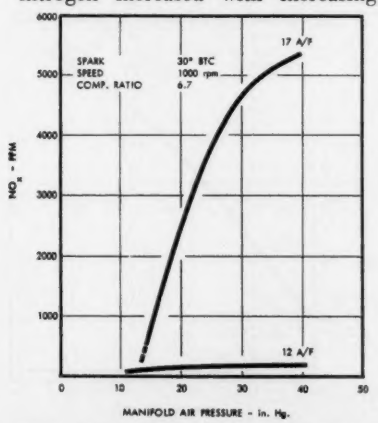


Fig. 6. Manifold air pressure cross-plot.

Engine Speed

The effect of engine speed on the concentration of oxides of nitrogen is complicated. With rich mixtures, higher concentrations were found at the higher engine speeds as shown in Fig. 7, whereas with lean mixtures the opposite was true. The speed effect was more pronounced in the lean mixture region. These results are cross-plotted in Fig. 8 at four different air-fuel ratios, to show the changing effect of engine speed. The maximum concentration of oxides of nitrogen decreased with engine speed, from about 4500 ppm. at 500 rpm. to 3900 ppm. at 3000 rpm.

Compression Ratio

Higher concentrations of oxides of nitrogen were found at higher compression ratios, other conditions being equal. Fig. 9 through 12 *(see page 217)* show data for compression ratios of 6.7, 9.5, and 12.0 to 1. These tests were all made at full load, but with different spark timing. In Fig. 11, the data shown for 12 to 1 compression ratio were obtained with light to moderate knock. This test series was not completed because of the possibility that knock, which became quite severe when the air-fuel ratios was made leaner than about 15, might damage the engine.

Cross-plots of the preceding data for an air-fuel ratio of 17 are shown in Fig. 13. The increase in concentration of oxides of nitrogen with increase in compression ratio seems to diminish as the compression ratio is raised.

A few tests were made at part load, 15 in. of mercury manifold air pressure. The results, shown in Fig. 14, *(see page 218)* suggest that compression ratio has a proportionately greater effect on the concentration of oxides of nitrogen at part load than at full load. This conclusion is based on limited data, however, and, therefore, is only tentative.

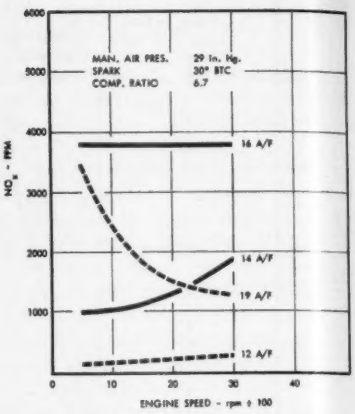


Fig. 7. Effect of engine speed on oxides of nitrogen.

Discussion

Arnoldi [3] investigated the effects of air-fuel ratio, compression ratio, and engine speed on the concentration of oxides of nitrogen in an ASTM - CFR Fuel Research Engine and with essentially the same analytical method as that used in this investigation. Unfortunately, he reported no spark timing data whatsoever. If Arnoldi maintained constant spark timing throughout his tests, his results are in essential agreement with those obtained during this investigation. He reported the same type of relationship between air-fuel ratio and oxides of nitrogen, the same increase in oxides of nitrogen with compression ratio under lean mixture conditions, and the same peculiar effect of engine speed. The only noticeable difference between the results of the two studies was that Arnoldi

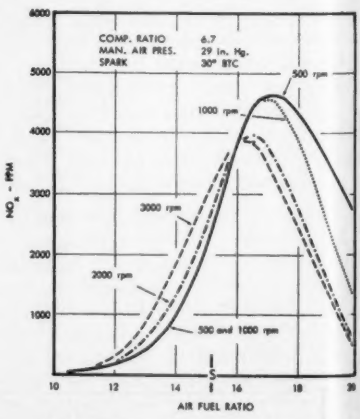


Fig. 8. Engine speed cross-plot.

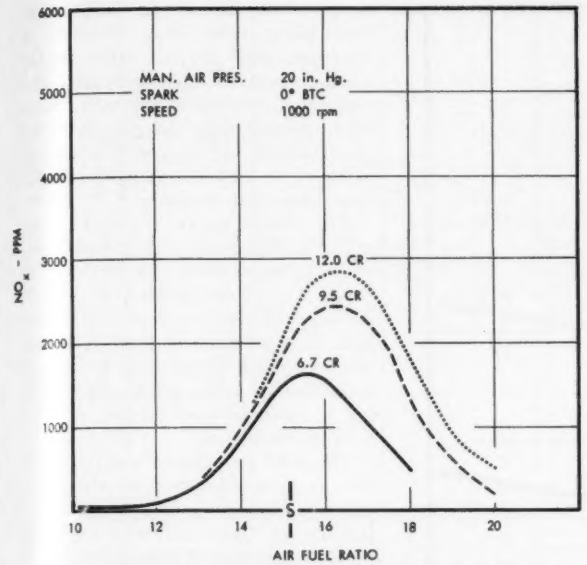


Fig. 9. Effect of compression ratio on oxides of nitrogen.

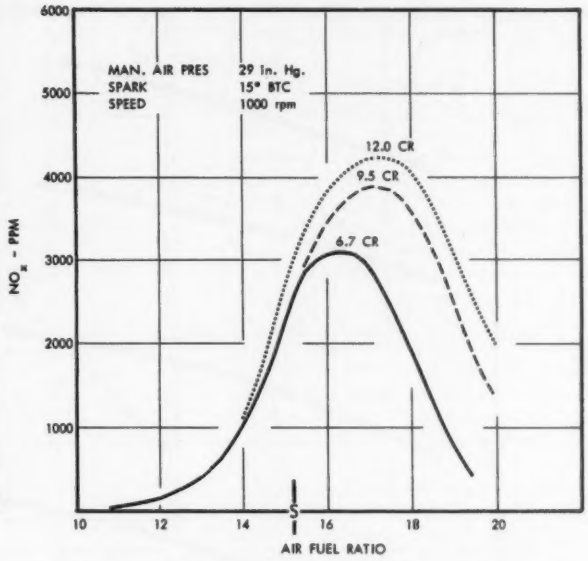


Fig. 10. Effect of compression ratio on oxides of nitrogen.

reported a somewhat greater effect of engine speed.

Spindt, Wolfe, and Stevens [5] investigated the effects of air-fuel ratio, spark timing, engine load, and engine speed on the concentration of oxides of nitrogen using a two-cylinder Gulf Test Engine. Although their analytical method for oxides of nitrogen was different from ours, results are believed comparable since both methods measure essentially all the oxides of nitrogen in exhaust gases. With one exception, these investigators found that engine variables affected oxides of nitrogen in nearly the same manner as in this study. The exception was spark timing. They reported that the concentration of oxides of nitrogen may decrease when the spark is advanced beyond the *optimum* setting, about 20° BTC under the conditions at which their experiments were carried out. This decrease was observed at air-fuel ratios of 13 and 16, but not at 18. In our investigation, advancing the spark always re-

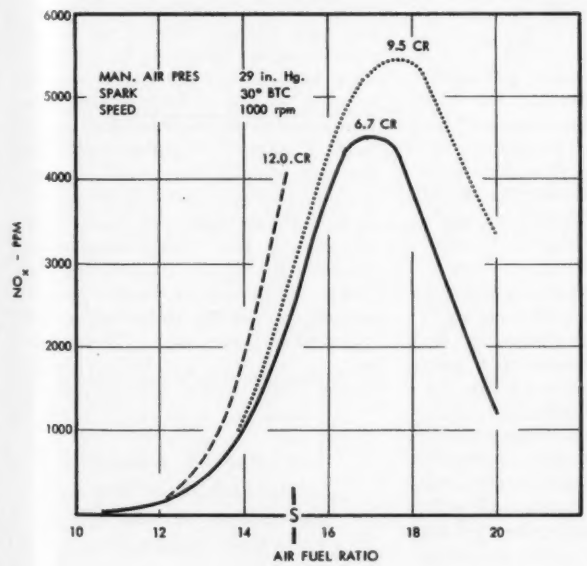


Fig. 11. Effect of compression ratio on oxides of nitrogen *(above)*.

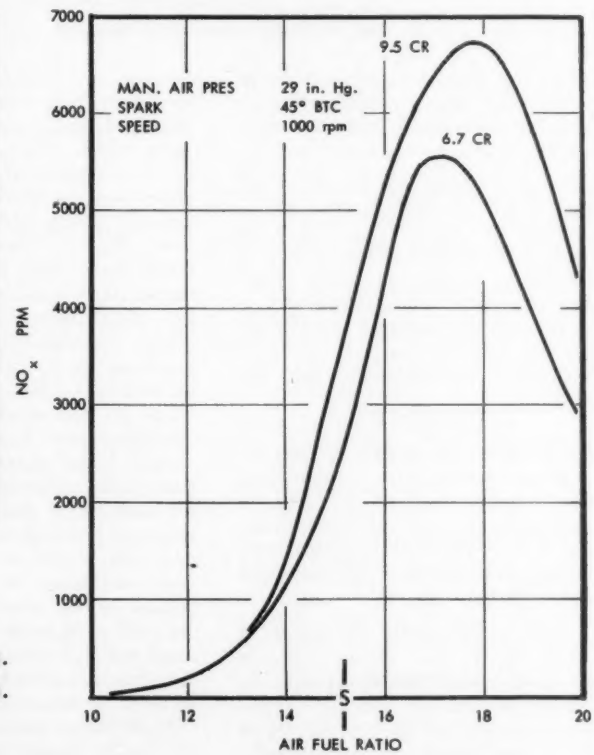


Fig. 12. Effect of cmpression ratio on oxides of nitrogen *(right)*.

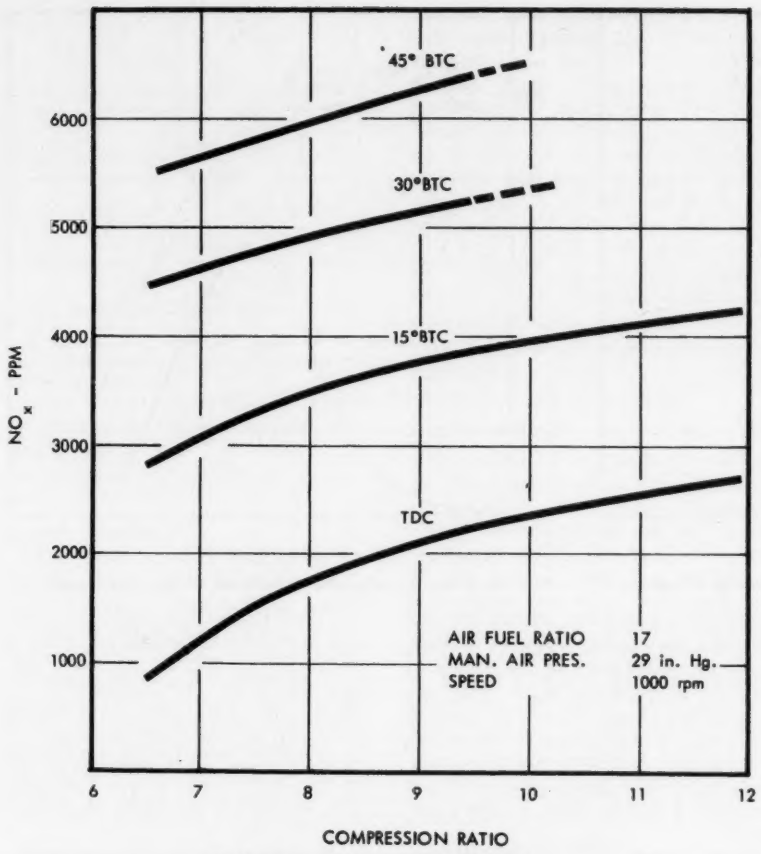


Fig. 13. Compression ratio cross-plot.

sulted in higher concentrations of oxides of nitrogen, although this effect was quite small with rich mixtures.

Exact analysis of the reactions leading to the formation of oxides of nitrogen in engine exhaust gases is impossible at present. However, it is possible to explain the effect of engine variables in a qualitative way by considering how each variable affects the time, temperature, and concentration of reactants for the reaction:

$$N_2 + O_2 = 2NO$$

The equilibrium constant for this reaction increases with temperature. The concentration of nitrogen in combustion gases changes very little, and for all practical purposes, only changes in oxygen concentration need be considered.

From a theoretical standpoint, it would appear that air-fuel ratio is the most critical engine variable, inasmuch as it affects both the oxygen concentration and the temperature of the combustion gases. Experimentally, oxygen concentration does seem to be the controlling factor in the rich mixture region, since engine variables which affect temperature but not gas composition do not materially change the concentration of oxides of nitrogen under rich-mixture conditions. Fig. 15 *(see page 219)* illustrates how peak cycle combustion temperature and oxygen concentration may vary with air-fuel ratio. While combustion temperature depends on many conditions other than air-fuel ratio, the curve in Fig. 15, based on calculated values[6], indicates the general trend. Similarly, the oxygen curve shows the concentration in the exhaust gases, which is not necessarily the concentration in the combustion gases at the time nitric oxide is formed. Under rich mixture conditions, the oxygen concentration in the combustion gases is believed to be dependent on air-fuel ratio and also to be considerably less than the 0.2 to 0.3% found in the exhaust gases.

Equilibrium concentrations of nitric oxide based on the values of temperature and oxygen concentration taken from Fig. 15 show a variation with air-fuel ratio similar to that observed experimentally. The calculated concentrations were, however, considerably greater than the experimental values, which is not unexpected in view of the many simplifying assumptions made.

The possibility was considered that either carbon monoxide or hydrogen, or both, might react with nitric oxide to an extent that significantly affects the net amount of nitric oxide formed. But since the rates of these reactions are very much slower than the rate of formation of nitric oxide, they were not considered significant in the present study.

Manifold air pressure and compression ratio are believed to affect the concentration of oxides of nitrogen because of their influence on peak cycle combustion temperature. Spark timing exerts its effect because it changes both the temperature of the combustion gases and, to some extent, the time available for the formation of nitric oxide. Reaction time, however, is influenced much less by spark timing than by engine speed.

The effect of engine speed on the concentration of oxides of nitrogen seems related to reaction time, but the reasons are much less apparent than with other engine variables. Under lean mixture conditions, higher concentrations of oxides of nitrogen were formed at lower engine speeds, possibly because of the increased time available for the formation of nitric oxide. Under rich mixture conditions, however, the opposite trend was observed. Higher concentrations were formed at the higher speeds. Perhaps the cooling rate of the combustion products during the expansion cycle, which is greater at higher speeds, was the controlling factor under rich mixture conditions. Wise and

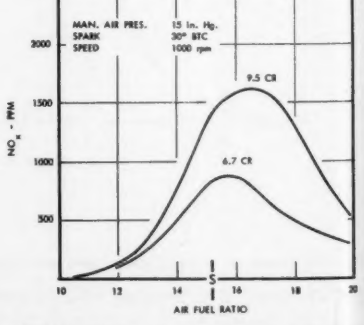


Fig. 14. Effect of compression ratio on oxides of nitrogen at part load.

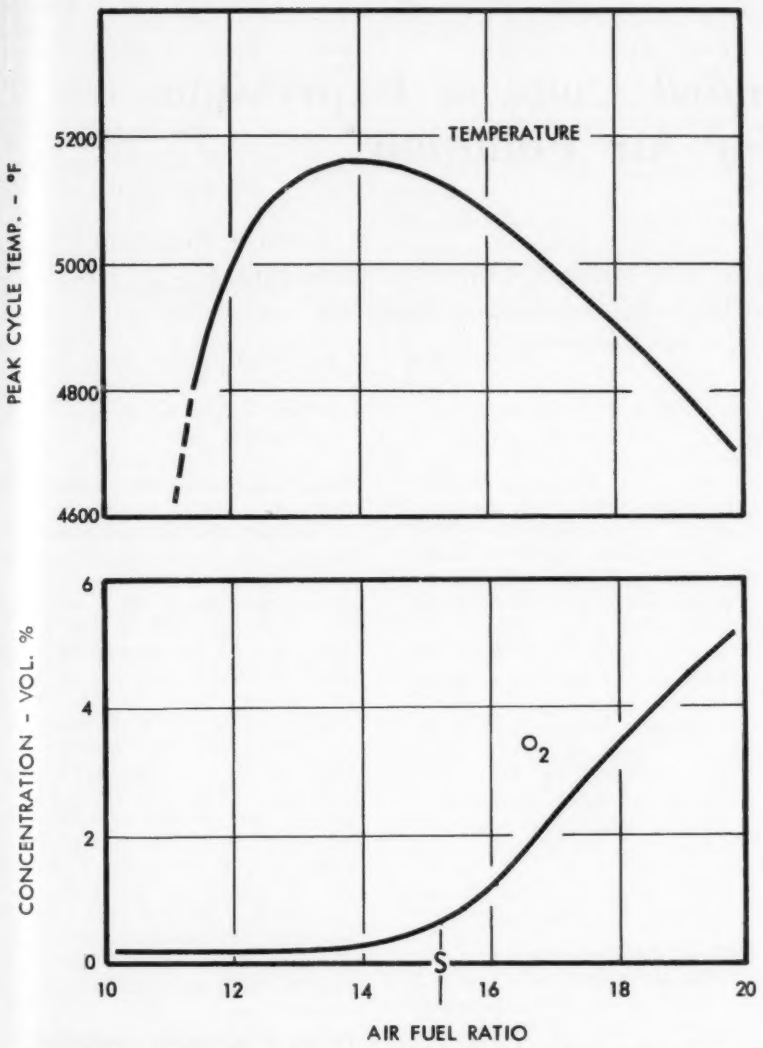


Fig. 15. Variation of peak cycle temperature and exhaust gas oxygen concentration with air-fuel ratio.

Baker [7] have reported that cooling rate significantly affects the yield of nitric oxide when equilibrium mixtures of nitric oxide and air are cooled rapidly from high temperatures.

Possible Methods for Controlling Oxides of Nitrogen in Automobile Exhaust Gases

The results of this investigation suggest that the concentration of oxides of nitrogen in automobile exhaust gases can be limited to a few hundred ppm. This result seemingly could be accomplished by carburetor modification to provide rich mixtures at all speeds and throttle settings. For best effectiveness, the air-fuel ratio should be between 11 and 12. Advantages of this approach are low first cost, ready adaptability to current and past model cars, and no extra maintenance or upkeep problems. Disadvantages include limited effectiveness, reduced fuel economy, and greater carbon monoxide emission. In a sense, this approach is like taking several steps backward because carburetors having these characteristics were in common use years ago.

Another approach is to retard spark timing. This appears less attractive than mixture richening, both because the gains seem more limited and because of the adverse effects on car performance as well as fuel economy.

Both of these control methods are among those under study in this laboratory.

Summary

The independent effects of air-fuel ratio, spark timing, manifold air pressure, engine speed, and compression ratio on the concentration of oxides of nitrogen in exhaust gases were investigated. Air-fuel ratio was found to be the most important variable. Maximum concentrations of oxides of nitrogen were formed when the air-fuel ratio was one to three ratios leaner than stoichiometric. The lowest concentrations, often only 1% of the maximum values, were found at the richest air-fuel ratios tested.

Advanced spark timing, higher manifold air pressures, and higher compression ratios favored the formation of oxides of nitrogen. The importance of these variables depended greatly, however, on air-fuel ratio. They had considerable effect under lean mixture conditions and little or no effect under rich mixture conditions.

The effect of engine speed was peculiar in that with rich mixtures, increasing speed favored the formation of oxides of nitrogen, whereas with lean mixtures, the opposite trend was found. Engine speed is considered the least important of the five variables investigated.

The effect of air-fuel ratio on the concentration of oxides of nitrogen is attributed to changes in oxygen concentration and, to a lesser extent, combustion temperature. The effects of spark timing, manifold air pressure, and compression ratio are believed to be due to their effects on combustion temperature. The effect of engine speed may involve the reaction time.

Two possible methods to reduce the emission of oxides of nitrogen from automobiles are pointed out. These involve modifications of carburetion or spark timing.

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Recommended Units of Expression for Air Pollution *

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At the present time, personnel engaged in the study of air pollution are confronted with the multitude of confusing and conflicting units of expression. A search through the literature has shown the wide variation in the methods of reporting data, presently in use. Many of the units of expression are carryovers from other fields of study, such as water pollution studies and industrial hygiene surveys. While these methods of expression are not incorrect, their application to air pollution studies is often misleading.

In this paper, a system of units of commonly measured parameters in the field of air pollution is presented. Many of the units currently in use are listed together with the recommended unit to be used. An attempt was made to reduce the number of units of expression to one for each of the parameters. Also, units were selected that would give small whole numbers for ease of handling and discussion. It will be noted that all values are expressed in the metric system.

The following criteria served as the basis for the selection of the recommended unit of expression:

(1) Units Actually Measured. Since most chemical analyses determine weight of material, units were selected within the dimensions actually measured. Weight of material is reported in grams, milligrams, or micrograms accordings to the fitness of one of these measures for other criteria being considered.

(2) Units Requiring No Extrapolation. Many units presently in use require extrapolation to extremely large areas or volumes, and the extrapolation factor introduced leads to either erroneous or misleading values.

(3) Uniform Units. To avoid the ambiguity whether reported values are on a weight or volume basis, units were selected to fit other criteria and at the same time would be applicable to particulate and gaseous materials.

(4) Practical Units. Units of expression were selected as far as possible to give the small whole numbers which facilitate reporting and discussion.

Particle Fallout

Units presently in use:

(1) tons per square mile per month
(2) tons per square mile per year
(3) pounds per acre per month
(4) pounds per acre per year
(5) pounds per thousand square feet per month
(6) ounces per square foot per month
(7) grams per square foot per month
(8) grams per square meter per month
(9) kilograms per square kilometer per month
(10) grams per month per 4 inch or 6-inch diameter jar
(11) milligrams per square inch per month

Recommended unit: milligrams per square centimeter per time interval as mg./sq. cm./mo. or mg./sq. cm./yr.

Range reported: 0.5 to 135 mg./sq. cm./mo.

The most common unit of expressing particle fallout rate, at present, is tons/mi.^{2}/month. This requires an extrapolation of 319 X 10^6 for a 4-in. jar and 142 X 10^6 for a 6-in. jar. Rather than include an extremely large factor, it is more practical to report the values in a unit dimension within the area actually measured. The recommended unit can also be applied to any method of collection whether it is by jar, tray, or adhesive surface. In reporting particle fallout, the type of sampling instrument should also be described, until an acceptable standard fallout sampler is developed. By reporting in common units, future development of sampling methods will make possible any needed corrections of past data.

Outdoor airborne particulate sampling

Units presently in use:

(1) milligrams per cubic meter
(2) parts per million by weight
(3) grams per cubic foot
(4) grams per cubic meter
(5) micrograms per cubic meter
(6) micrograms per cubic foot
(7) grains per cubic foot
(8) pounds per thousand cubic feet

Recommended Unit: Micrograms per cubic meter.

Range expected: 10 to 5000 micrograms per cubic meter.

The recommended unit of expression is the unit most commonly in use at the present time. The method

*Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers, The State University, Department of Sanitation, New Brunswick, N. J.

of sampling must also be mentioned with the reported data. With a uniform expression of results, reported data can be corrected by application of a simple factor.

Gaseous Materials

Units presently in use:
(1) milligrams per cubic meter
(2) micrograms per cubic meter
(3) micrograms per liter
(4) parts per million by weight
(5) parts per million by volume
(6) parts per hundred million
(7) parts per billion by weight or volume
(8) ounces per cubic foot
(9) pounds per cubic foot
(10) grams per cubic foot
(11) pounds per thousand cubic feet

Recommended unit: Micrograms per cubic meter.
Ranges reported: Depends on the specific gas.

The recommended unit was selected for conformity and uniformity and also is used in reporting airborne particulate results. Not only will similar methods of expression remove some confusion, it will also eliminate the need for converting one system of units to another. At the present time, methods used for sampling gaseous contaminants are not specific for gases and can collect the specific compounds in the particulate form.

Standard conditions for reporting Gas Volumes

Units presently in use:
(1) 760 millimeters Hg pressure and 20°C
(2) 760 millimeters Hg pressure and 0°C
(3) 760 millimeters Hg pressure and 65°F
(4) 700 millimeters Hg pressure and 0°C
(5) 700 millimeters Hg pressure and 20°C
(6) 30 inches of mercury pressure and 65°F

Recommended units: 760 millimeters Hg pressure and 10°C.

Although the recommendation may seem the addition of one more set of conditions for describing a standard volume, the recommended conditions more closely represent those found in air pollution studies.

Particulate counting

Units presently in use:
(1) number per cubic meter of gas
(2) number per liter of gas
(3) number per cubic centimeter of gas
(4) number per cubic foot of gas

Recommended unit: Number of particles per cubic meter of gas as million particles per cubic meter.
Range reported: 10 million and above particles per cubic meter.

Temperature.

Units presently in use:
(1) degrees Centigrade
(2) degrees Farenheit

Recommended unit: Degrees Centigrade.

Time

It is recommended that time be measured on the 0000 to 2400 basis to eliminate the possibility of confusion that results from two 12 hr. (a day) sections.

Pressure

Units presently in use:
(1) atmospheric pressure
  a. atmospheres
  b. millimeters of mercury
  c. inches of mercury
  d. millibars
(2) sampling pressures
  a. millimeters of mercury
  b. inches of mercury
  c. millimeters of water
  d. inches of water

Recommended unit: millimeters of mercury.

In spite of the fact that a great many pressure and vacuum gauges are scaled in the English system as in. of water, it is believed that uniformity would be better served if pressure conditions are expressed in mm. of mercury.

Linear Velocity

Units presently in use:
(1) meters per second
(2) *meters per hour*
(3) kilometers per hour
(4) feet per second
(5) feet per minute
(6) feet per hour
(7) miles per hour
(8) meters per minute
(9) centimeters per second

Recommended unit: meters per second.
Example range: 0 to 100 meters per second.

From the range reported, the recommended unit can be seen to offer a parameter which will cover a wide variation in linear velocities without becoming unwieldy and cumbersome. Even hurricane velocities of 225 mi./hr. can be expressed in the recommended unit of 100.6 m./sec.

Volume emission rates

Units presently in use:
(1) cubic meters per hour
(2) cubic meters per minute
(3) cubic meters per second
(4) cubic feet per hour
(5) cubic feet per minute
(6) cubic feet per second

Recommended unit: cubic meters per minute.
Range expected: 1.5 to 300 cubic meters per minute.

The recommended unit allows an expression of relatively low emission rates through extremely high ones. The emission from small blowers as well as large stacks can be expressed with equal ease through the use of this parameter.

Sampling rates

Units presently in use:
(1) cubic meters per second
(2) cubic meters per minute
(3) cubic feet per second
(4) cubic feet per minute
(5) liters per second
(6) liters per minute
(7) cubic centimeters per second
(8) cubic centimeters per minute

Recommended units:
cubic meters per minute
cubic decimeters per minute
cubic centimeters per minute

Ranges reported: From cubic centimeters per minute to 3 cubic meters per minute.

The selection of cubic meters, cubic decimeters, or cubic centimeters will depend on the sampling equipment used, and the expression of the rate chosen should give small whole numbers.

Instantaneous light transmission studies

Units presently in use:
(1) percent reduction per mile (visibility)
(2) percent reduction per 1000 feet (photoelectric)
(3) percent reduction of emitted light
(4) percent transmitted

Recommended unit: percent transmitted.
Range expected: 0 to 100%.

Until the adoption of standard techniques for light transmission studies, reports containing these data should include a description of the physical plan used, for example, strength of light source and length of light path. With the variety of arrangements presently in use, the only correct value that is obtained is actual light transmitted for each installation.

Visibility

Units presently in use:

(1) miles and fractions of a mile

(2) kilometers and fractions of kilometers

Recommended unit: kilometers.

Particle count on sedimentation devices (both horizontal and vertical).

Recommended unit: Number of particles per square centimeter per time interval.

Weight of particulate matter on sedimentation devices (horizontal and vertical).

Recommended unit: Milligrams per square centimeter of surface per sampling interval.

The sedimentation devices considered here include adhesive papers, greased plates, dry plates, and other such collection surfaces that do not use a liquid as the collecting medium. The unit of expression should be the same as for the particle fallout even though the collection efficiencies of the sedimentation devices are not exactly the same. Uniformity of reporting may stimulate study of the efficiencies of collection of the different sedimentation devices.

Summary

A system of recommended units of expression has been presented for use in the air pollution field. In addition to exclusive use of the metric system the units were selected according to the following criteria: use of dimensions actually measured; units that require no extrapolation, and units as nearly uniform as possible; and practical units.

Following these limits the units of expression selected are:

Particle fallout Milligrams per square centimeter per time interval.

Outdoor airborne particulates Micrograms per cubic meter.

Gaseous material Micrograms per cubic meter.

Gas volumes reported at 760 millimeters Hg pressure and 10°C.

Particulate counting Number per cubic meter.

Temperature Centigrade scale.

Time 0000 to 2400 hours per day.

Pressure Millimeters of mercury.

Linear velocity Meters per second.

Volume emission rates Cubic meters per minute.

Sampling rates Cubic meters, cubic decimeters, or cubic centimeters per minute.

Instantaneous light transmission Percent transmitted.

Visibility Kilometers.

Particle count on sedimentation devices Number of particles per square centimeter per time interval.

Particle weight on sedimentation devices Milligrams per square centimeter per time interval.

It is believed that adoption and use of the recommended units of expression will result in a uniformity of reporting and removal of the confusion that is now found in studies of air pollution. A uniform system of reporting will demonstrate a wide variation in results obtained in sampling for the same material by different methods. This in turn may indicate the path that should be taken by research groups, and in fact, the entire field, to bring about acceptable methods for the measurement of materials present in the atmosphere.

System Designs for the Catalytic Decomposition of Nitrogen Oxides

(Continued from page 212)

phere from a nitric acid plant. Other factors such as total vol. and weather conditions undoubtedly influence the lower visible detection level.

Analytical results have been made available by users which indicate reductions to below 160 ppm. residual oxides of nitrogen leaving the system, with over 5000 ppm. entering, and with substantial amounts of free oxygen remaining in the effluent. Logically, any reporting of results should be accompanied by a description of the analytical methods employed. However, since the accuracy of the methods so far used are subject to question, and since there appears to be disagreement regarding the reliability of various methods, analytical procedures have been excluded from the scope of this paper.

Catalyst life obviously has an important bearing on the expanded use of the process. Elements which have been in use without service for twelve months are continuing to produce a color-free effluent. Washing procedures extend the permissible duty, and eventually the catalyst can be reactivated at a small fraction of its original cost. Evidence to this time indicates that life expectancy may exceed 20,000 operating hrs., as is common when catalysts are used for the combustion of hydrocarbon vapors.

Conclusions

In the catalytic reduction of nitrogen oxides, no effort has been made to determine the influence of pressure on the reaction rate. The decision to accomplish reduction at elevated pressures, when possible, is based solely on the ability to secure profitable shaft power while dispensing with the conventional steam generating cycle. However, where the vol. of fumes requiring treatment at atmospheric pressure justifies heat recovery, waste heat boilers can undoubtedly be utilized to obtain partial returns for corrective costs.

Emphasis on existing installations has been placed on the correction of toxic and corrosive hazards associated with industrial off-gas containing exceedingly high concentrations of nitrogen oxides. Experimental installations are now being made where nitrogen oxide concentrations entering the system are expected to be less than 200 ppm. When a widely accepted method for testing and analysis is available, it is expected that data on the catalytic reduction of low concentrations can be offered.

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Control of Vapors from Bulk Gasoline Loading*

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County of Los Angeles

Los Angeles, California

Introduction

Approximately eight per cent of the total crude petroleum refining capacity of the United States, equivalent to some 750,000 barrels daily [1], is centered in Los Angeles County. Nearness to a crude petroleum supply, a large local market and marine transport have contributed to the growth of the petroleum industry in Southern California. Over 85% of the 750,000 barrels/day of crude petroleum capacity is located in the refineries of six major oil companies, with the remaining 15% in the refineries of twelve independent oil companies, as shown in Table I.

Production of gasoline alone, by these refineries, approximates 15 to 16 millions of gallons daily, of which an estimated 5,500,000 are sold to fuel the 2,800,000 motor vehicles registered within Los Angeles County. The balance of the gasoline manufactured is transported by tanker, tank car, tank vehicle and pipeline to airports, military bases, and other consumers, both locally, and in other parts of California and the adjoining Western states.

The distribution of gasoline to the ultimate consumer is accomplished by a network of pipelines and tank vehicle transfer routes from the refineries to the consumer outlets. Integrated into this network are intermediate locations with separate storage facilities and tank vehicle loading equipment. These are referred to as bulk terminals, if supplied by pipelines from the refineries, or as bulk plants, if supplied by tank vehicles from the refineries or bulk terminals. Aircraft fuel tanks are filled from tank vehicles working out of airport bulk plants, some of which are supplied by pipelines and some by tank vehicles. Deliveries to marine terminals for tanker shipments are made by pipelines from the refineries.

A recent survey showed 98 separately located loading facilities at refineries, bulk terminals and bulk plants, and 15 at airports, which were used for filling tank vehicles. Of the total gasoline gallonage loaded out by these 113 installations, about 90% is from the 27 refinery and bulk terminal locations. Table II contains further details on this subject. There are, in addition, about 7500 retail service stations and 10,000 consumer account outlets which are mostly supplied from tank vehicles.

Production of Vapor Losses

When a tank vehicle, or a compartment of a tank vehicle, is filled through an open hatch, the incoming liquid displaces the vapors present in the compartment into the atmosphere. Except in rare instances, where a tank vehicle is being used for the first time, or immediately after a gas-freeing, the displaced vapors are a mixture of air and hydrocarbons. These vapors vary in hydrocarbon concentration and composition depending upon the product being loaded, the temperature of the product and of the tank vehicle, and the type of loading. Ordinarily, but not always, the hydrocarbon concentrations of the vapors are in the range of 30 to 50% by volume and consist

TABLE I

Crude Oil Capacities of
Los Angeles County Petroleum Refineries*

Refinery name	Approximate crude throughput (barrels/day)
1. Richfield Oil Corporation	130,000
2. Standard Oil Company of California	130,000
3. General Petroleum Corporation	125,000
4. Union Oil Company of California	125,000
5. Shell Oil Company	80,000
6. The Texas Company	60,000
7. Wilshire Oil Company of California	25,000
8. Hancock Oil Company	15,000
9. Rothschild Oil Company	10,000
10. Sunset International Petroleum Corporation	9,000
11. Macmillan Petroleum Corporation	8,000
12. Edgington Oil Refineries, Inc.	7,000
13. Douglas Oil Company of California	6,000
14. Century Oil Company	5,000
15. Fletcher Oil Company	5,000
16. Manespo Refining Company	4,000
17. Envoy Petroleum Company	3,000
18. Newhall Refining Company	3,000
19. Calstate Refining Company	**
Total	750,000

*Knudsen, Edward T., *Petroleum Refineries, Cracking Plants, Natural Gasoline Plants and Cycling Plants in District 5*, U. S. Department of Interior, Bureau of Mines, January 1, 1956.

**Cracking plant only; no crude oil processed.

*Presented at the 50th Annual Meeting of the Air Pollution Control Association held at St. Louis, Mo., June 2-6, 1957.

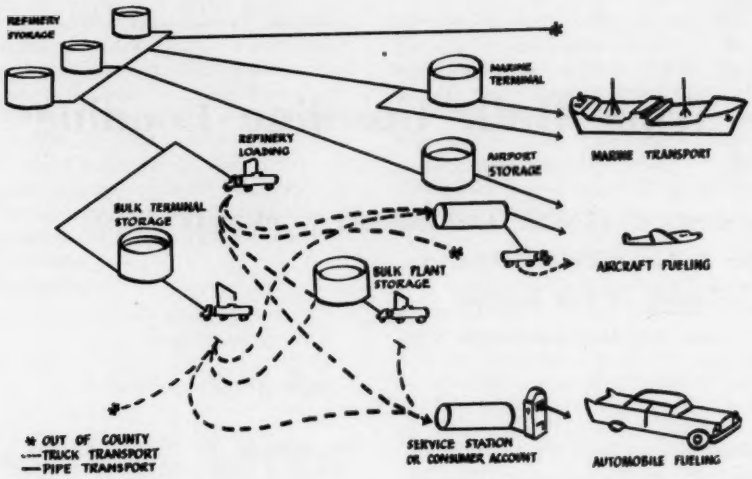

Fig. 1. Representation of Gasoline Distribution System in Los Angeles County, showing flow of gasoline from refinery to consumer.

of gasoline fractions ranging from propane through hexane. In Table III, a typical analysis is given for the vapors emitted during the loading of tank vehicles with motor gasoline.

The production of vapor during the loading of a tank vehicle, as well as its composition, is greatly influenced by the type of loading or filling employed. These types can be classified as splash, submerged or bottom filling. In splash filling, the outlet of the filling tube is above the liquid surface during all or most of the loading. In submerged filling, the filling tube is extended to within six inches of the bottom and is submerged beneath the liquid during most of the loading. Bottom filling is achieved through connecting a loading hose to a nozzle below the liquid surface of the tank. Bottom filling has been encountered only at aircraft fueling stations and LPG loading racks because of the costs of conversion and large investments in existing equipment.

Splash filling generates more turbulence and therefore more hydrocarbon vapors than does submerged filling, other conditions being the same. Vapor losses from the filling of tank vehicles with gasoline were determined experimentally to be from 0.1 to 0.3% of the volume loaded.[2,3] Fig. 2 presents a correlation of loading losses with gasoline vapor pressures. It was determined by inspection that most of the loading racks supposedly employing submerged filling actually operated in such a manner that the resulting filling was half splash.

Using six million gallons as the amount of gasoline loaded daily into tank vehicles in Los Angeles County, a calculation based on the experimental evidence showed that hydrocarbon vapor losses could be between 15 to 45 tons a day. From inspection of the loading operations, these losses from uncontrolled loading into tank vehicles were estimated to be about 30 tons a day. The losses from loading tank ships, tank cars, service station tanks and automobiles added another 60 tons for a total of about 90 tons a day. In addition to the losses resulting from the displacement of hydrocarbon vapors from the tank vehicles, inspections revealed additional hydrocarbon losses due to evaporation from gasoline spillage, drainage and leakage attending some loadings. On a few occasions the losses from spillage and overfilling may have exceeded the displacement losses.

In view of the established importance of hydrocarbons to smog formation,[4, 5, 6, 7] and field surveys which indicated that losses from this source were more than just a few tons/day, control of vapor emissions at key points in the distribution system seemed justified.

This conclusion received more support as controls were completed for hydrocarbon vapor emissions from storage and various phases of refining. By 1954, the 30 tons/day of hydrocarbons displaced from tank vehicles during bulk gasoline loading became relatively more significant. Unfortunately, methods of control for this source were not in existence.

Initiation of Development of Controls

Recognizing that the controlling of vapors from bulk gasoline loading was a mutual problem, the District

TABLE II

Bulk Gasoline Loading in Los Angeles County
February 1955 (Prior to Installation of Controls)

Class	Number of installations	Throughput gal./month	% Total throughput
Major Refinery or Bulk Terminal	22	143,674,700	83.4
Independent Refinery	5	12,163,000	7.1
Aircraft Fueling Facility	15	6,065,300	3.5
*Small Bulk Distribution Plant	71	10,339,600	6.0
Total	113	172,242,600	100.0

*Each facility handles less than 20000 gal./day.

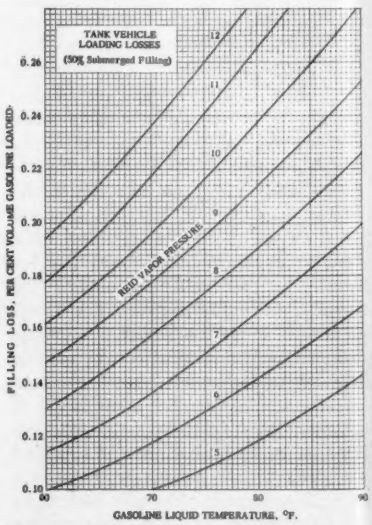

Fig. 2. Correlation of tank vehicle loading losses (50% submerged filling) with reid vapor pressure and liquid temperatures of the motor gasoline.

TABLE III

Typical Analysis of Vapors From Bulk Loading Motor Gasoline Into Tank Trucks

Fraction		Mol. %		Weight %
Air		58.1		37.6
Hydrocarbon				
Propane	0.6		0.6	
Iso-Butane	2.9		3.8	
Butene	3.2		4.0	
N-Butane	17.4	41.9	22.5	62.4
Iso-Pentane	7.7		12.4	
Pentene	5.1		8.0	
N-Pentane	2.0		3.1	
Hexane	3.0		8.0	100.0
		100.0		

encouraged members of the petroleum industry to undertake development of controls on a voluntary basis. Under this approach, vapor collectors for the loading tubes, vapor disposal systems, and new type loading arm assemblies were designed and built despite the many problems which arose; for example, hatch openings were not uniform, and loading arm assemblies were not standardized.

After construction and operation of some pilot control equipment, the drafting of a Rule to require controls on bulk gasoline loading was initiated. The magnitude of the operation, the type of products handled, the transportation equipment used, and the degree of control efficiency were all considered in the preparation of the Rule.

Resolution of these issues and installation of some control systems was achieved in the early part of 1956. Rule 61 was adopted and became effective March 8, 1956. This Rule states:

Rule 61. Gasoline Loading Into Tank Trucks and Trailers

A person shall not load gasoline into any tank truck or trailer unless hydrocarbon vapor or gas loss to the atmosphere is prevented by a vapor collection and disposal system or its equivalent, properly installed, in good working order, and in operation.

When loading is effected through the hatches of a tank truck or trailer with a loading arm equipped with a vapor collecting adaptor, a pneumatic, hydraulic or other mechanical means shall be provided to force a vapor tight seal between the adaptor and the hatch. A means shall be provided to prevent liquid gasoline drainage from the loading device when it is removed from the hatch of any tank truck or trailer, or to accomplish complete drainage before such removal.

When loading is effected through means other than hatches, all loading and vapor lines shall be equipped with fittings which make vapor tight connections and which close automatically when disconnected.

The vapor disposal portion of the system shall consist of one of the following:

a. A vapor-liquid absorber system with a minimum recovery efficiency of 90% by weight of all the hydrocarbon vapors and gases entering such disposal system.

b. A variable vapor space tank, compressor, and fuel gas system of sufficient capacity to receive all hydrocarbon vapors and gases displaced from the tank trucks and trailers being loaded.

c. Other equipment of equal efficiency submitted to and approved by the Air Pollution Control Officer.

For the purpose of this rule, any petroleum distillate having a Reid vapor pressure of four lb. or greater shall be included by the term "gasoline".

This rule shall not apply to the loading of gasoline into tank trucks and trailers, from any loading facility where not more than 20,000 gallons of gasoline are loaded in any one day.

For the purpose of this rule, "loading facility" means all gasoline loading equipment which is both (1) possessed by one person, and (2) located upon a single parcel of land or upon contiguous parcels of land.

(For clarification, it is now proposed to amend the last paragraph of Rule 61 as follows: "For the purpose of this rule, 'loading facility' means any aggregation or combination of gasoline loading equipment which is both (1) possessed by one person, and (2) located so that all the gasoline loading outlets for such aggregation or combination of loading equipment can be encompassed within any circle of 300 feet in diameter.")

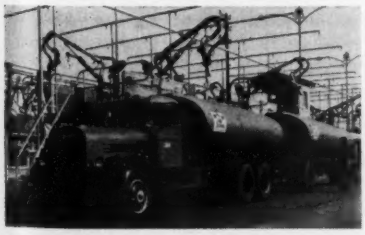

Fig. 3. An open overhead controlled loading rack showing greenwood vapor closures on the pneumatically operated loading arms.

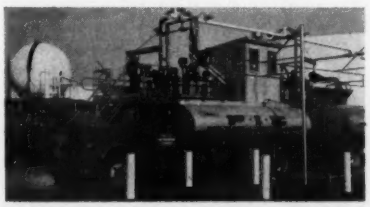

Fig. 4. An open overhead controlled loading rack showing spring operated loading arm, SOCO vapor closure, preset stop meters and vapor disposal system (absorption) in background.

Loading Racks

The facilities by which gasoline is transferred into tank vehicles from the product storage tanks are located at structures known as loading racks. These racks, in Los Angeles County, are raised platforms to which the various products are piped and at which these pipelines terminate in loading equipment so constructed as to deliver gasoline into the tank vehicles through their top hatches. (Fig. 3 and 4). Sizes of loading racks vary in accordance with the number of products to be loaded and trucks to be accommodated. The platform structure is generally constructed with hinged side platforms, attached to the sides of a central walkway, that can be raised when not in use. Thus, a tank vehicle is able to park close to the central walkway for loading and the hinged side platforms can be lowered to rest upon the top of the tank vehicle and provide an access to the compartment

hatches. Metal canopies on some of the racks restricted the amount of overhead space and thus affected the design of the loading assemblies and,

Fig. 5. An overhead controlled loading rack with canopy.

thereby, the type of vapor collection (Fig. 5).

Loading Arm Assemblies

The term, "loading arm assembly", refers to the equipment and appurtenances at the discharge end of a product pipeline which is used in filling an individual tank vehicle compartment. This can include the piping, valves, meters, swivel joints, fill spouts and vapor collector adapters and is sometimes abbreviated to "loading arm". (See Fig. 6 and 7.). Loading arms of presently controlled racks can be classified in accordance with how vertical movement of the loading arm is achieved, either as pneumatic, counter-weighted or torsion-spring. The pneumatically operated arm is a successor to the common spring-loaded automatic locking arm in which the spring loaded cylinder has been replaced by an air cylinder (Fig. 8).

In designing for complete vapor pickup at the tank vehicle hatch, it was necessary to consider many factors: tank settling, liquid drainage, and "topping-off". The settling of a tank vehicle due to the weight of product being added introduced the problem of providing for vertical travel of the loading arm to follow the vehicle motion so that the vapor collector would remain sealed in the

Fig. 6. View of uncontrolled loading operation showing the horizontal swing-type loading arm, outboard loading valve, and detachable drop tube.

tank hatch during the entire loading operation. The amount of liquid drainage from a loading arm withdrawn after filling was found to depend upon the location of the loading valve. Elimination of the common practice of "topping-off" a compartment was also judged desirable by the District. "Topping-off" is the term for the last phase of the loading operation in which the level of the liquid is adjusted to the compartment capacity marker [8] with the loading arm partially out of the tank vehicle hatch. During such op-

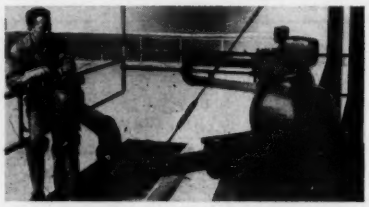

Fig. 7. View of uncontrolled loading operation showing the horizontal swing-type loading arm, visual meter, outboard loading valve and detachable drop tube.

eration, vapor pickup in the vapor collector would be nil.

For the problem of tank vehicle settling, two solutions were used. In one, air pressure, continuously applied to the piston in the air cylinder of the pneumatically operated loading arm, forced the loading arm to follow the motion of the tank vehicle without clamping or fastening of the vapor collector to the tank vehicle. In the other, for counterweighted and torsion spring loading arms, the design and operation of the SOCO [9] vapor closure effectively locked the loading arm into the tank vehicle hatch so that it would follow the motion of the tank vehicle.

For the problem of liquid drainage, two solutions were adopted. Inspection of assemblies having the valve at the outboard position, (directly over fill stem) showing adequate drainage could be accomplished by adjusting the withdrawal rate of the assembly, was the key to the first solution for pneumatic loading arms. The valve which operated the air cylinder was modified to allow 30 to 45 sec. to elapse before the assembly cleared the hatch compartment. This modification was made by the addition of an orifice in the discharge side of the air valve. Loading arms with inboard valves required additional drainage time and also presented the problem of gasoline retention in the horizontal part of

Fig. 8. Close-up view of a controlled pneumatically operated loading arm showing air cylinder, remote reading meter, outboard loading valve, air cylinder controls, pantograph linkage, modified greenwood vapor closure and vapor hose.

the arm. Installation of a spring-loaded valve located in the tip of the filling stem solved both problems. A 20 to 30-lb. pressure setting was satisfactory in preventing most of the drainage even though thermal expansion of the gasoline caused by absorption of heat from the sun was sufficient to open the valve partially. Addition of a small surge chamber equipped with a vacuum breaker in place of the usual vacuum breaker on the loading valve corrected this situation. For the second solution, applicable to counterweighted and torsion spring loading arms, the SOCO vapor closure was used which was positioned at the bottom of the loading tube and which was equipped with an internal shut-off valve actuated whenever the loading arm is withdrawn from the tank hatch.

The custom of open "topping-off" follows from the necessity of having loads meet the regulations of the Los Angeles County Department of Weights and Measures. These regulations established a system of calibrated capacity markers in each tank compartment which guaranteed the volume loaded. The California State Highway Department, however, does not use the markers for determining overload of vehicles but rather relies on acutal weighing. Oil companies delivering exclusively to their own retail outlets found it more practical to meter the desired volumes. In this practice, loading must be restricted to empty trucks or to trucks prechecked for loading volume available. Accuracy of certain totalizing meters or preset stop meters has proved satisfactory for loading without the need for subsequent open "topping". An interlock device for the pneumatic type loading arm, consisting

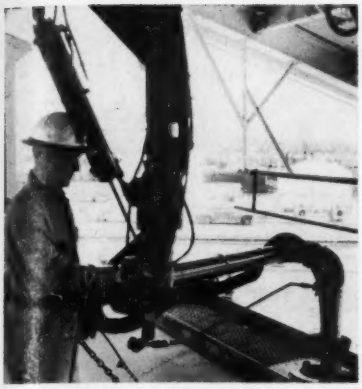

Fig. 9. Close-up view of a controlled pneumatically operated loading arm showing air cylinder, inboard loading valve, greenwood vapor hose, closure, vapor hose, pantograph linkage and filling stem.

of pneumatic control or mechanical linkage, prevents the loading valve from being opened unless the air cylinder valve is in the "down" position so that open "topping" is theoretically impossible.

A connecting rod between the riser and filling stem has been added on some assemblies to form a pantograph arrangement to maintain the filling stem of the loading arm in a vertical position at all times (Fig. 9). The loading operator is thus able to obtain good sealing contact more quickly and readily between the collector and the hatch opening.

Vapor Closures

Three types of vapor collectors or closures, fitting the loading tube, have been developed — the General Petroleum Corporation unit, the Vernon Tool Company or Greenwood unit, and the SOCO unit. All are essentially plug-type devices with a central channel through which gasoline can flow into the tank vehicle compartment. This central channel, actually a section of the loading tube, is surrounded by an annular vapor space. Entry into this vapor space is achieved through openings located in the bottom portion of the plug, which portion will be below the point of contact between the sides of the plug and the hatch opening. Thus, vapors are prevented from passing around the plug and out of the hatch and must flow instead into the annular space, or vapor chamber, which in turn is connected to a vapor hose or pipe leading to a vapor disposal system.

The vapor closure device developed by the General Petroleum Corporation has an auxiliary, transparent, plexiglass vapor chamber section above the plug to give the operator observability of the calibrated capacity markers. A neoprene rubber bellows above the plexiglass chamber compensates for vertical misalignment of the plug in the hatch opening. The plug is aluminum, cast in the shape of a truncated cone. The lateral surface of the plug is faced with a neoprene rubber gasket in the shape of a spherical section so as to give a vapor tight seal between the closure and the hatch when the closure is positioned in the hatch for loading. The top of the closure has openings for the loading tube and the vapor take-off line. An adjustable slip ring serves as a positioner enabling the loading operators to slide the closure to the proper height on the loading tube for various depths of tank vehicle compartments. Such a closure requires a constant downward force to keep it in contact with the compartment hatch opening sides at all times during filling and is built to fit only 8 to 10″ dia. hatches. (See Fig. 10.)

The second type of closure, the Greenwood Unit, (Fig. 8 and 9) also requiring a downward force during the filling operation was developed by the Vernon Tool Company. This closure is also of cast aluminum with a plug of similar shape to the General Petroleum closure and with a neoprene rubber gasket. This closure has no auxiliary transparent vapor chamber section although some versions of this closure do have auxiliary metal vapor chambers. It fits tank truck compartments with hatches from 8″ to 10″ in dia. Since compartments with hatches of larger diameters are sometimes encountered, an adapter has been provided. The adapter consists of a flat, gasketed plate with an 8 in. dia. hole in the center through which the closure can be inserted.

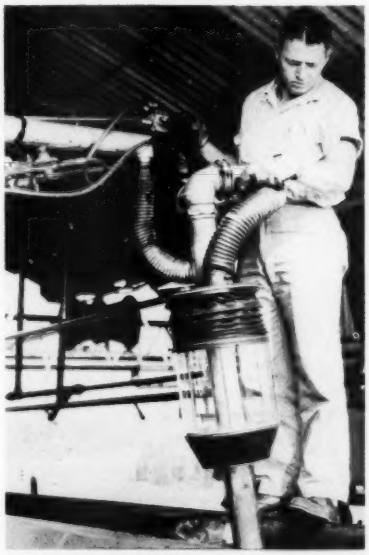

Fig. 10. Close-up view of general petroleum corporation vapor closure on a pneumatically operated loading arm. Plexiglass vapor chamber, bellows, tapered plug, vapor hose and air controls as shown.

Fig. 11. Close-up view of SOCO vapor closure.

The third type of vapor closure (Fig. 11, 12 and 13), referred to as SOCO, was developed by Standard Oil Company of California and consists of an aluminum cast plug of more complicated design. This closure is locked into the hatch opening by a cam lever device which forces a floating internal cylindrical section

Fig. 12. View of loading operation with a SOCO vapor closure on a counterweighted loading arm showing cam lever locking device and vapor hose.

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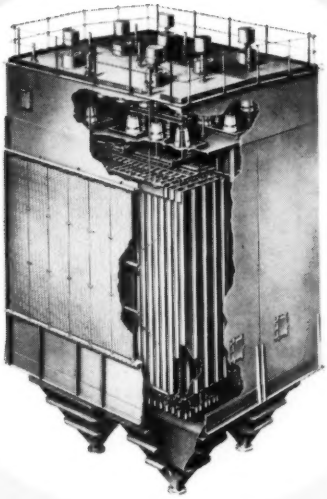

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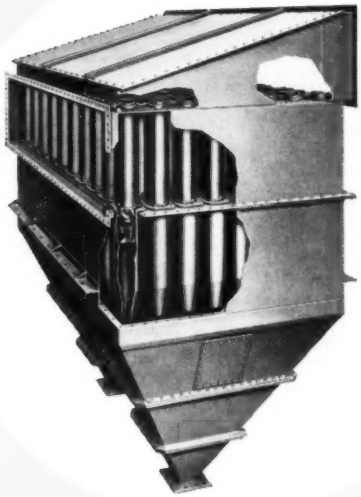

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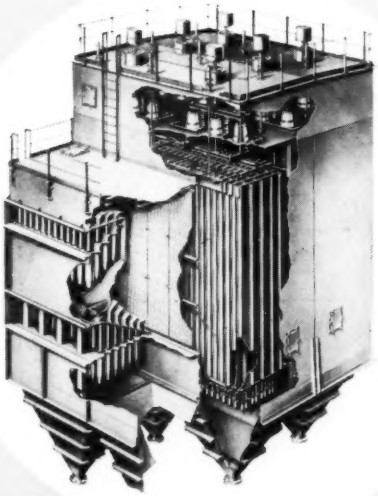

Combination
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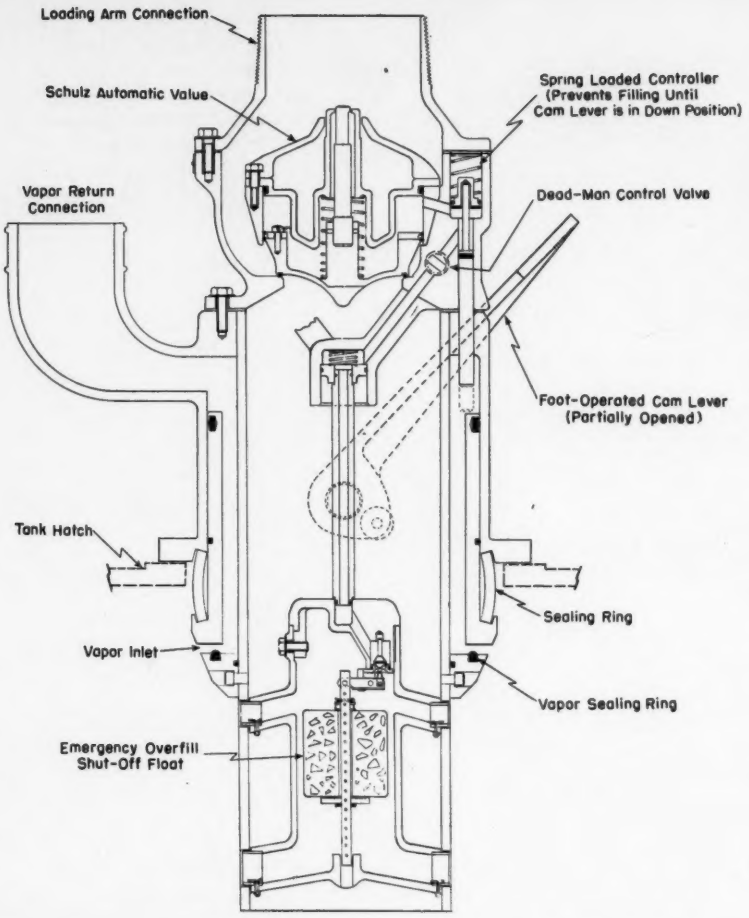

Fig. 13. Schematic drawing of a SOCO vapor closure used to collect displaced vapors during loading.

to roll upwards, squeezing a neoprene rubber collar out against the sides of the hatch opening, thus effecting a vapor-tight seal during all phases of loading. As the floating, internal cylindrical section is rolled upwards by the action of the cam lever device it exposes the vapor entry opening. A diaphragm operated, internal filling valve, similar to an aircraft fueling valve was developed for this closure. A needle pilot valve and a safety shutoff float operate the internal valve to prevent overfilling. The closure automatically seals off the vapor side on removal from the hatch and prevents any leakage from the vapor-gathering lines. SOCO closures fit 8 in. dia. hatches only, although an adapter has been developed for hatches 10 in. in dia. This adapter is a circular casting with an 8 in. opening which is placed over the hatch opening. When the SOCO unit is inserted, spring-loaded arms act to clamp and seal the adapter against the top of the hatch.

Inspections have shown that the General Petroleum closure and the Greenwood closure require nearly vertical entry of the loading tube into the compartment hatch opening in order to provide a tight seal against vapor leaks.

The slide positioner of the General Petroleum vapor closure, although permitting adjustments for submerged loading, can also be a source of vapor leaks and requires proper attention by the operator. SOCO closures with inner valves are considerably heavier than other types and the inner valve slows the loading rates. Both the Greenwood and the General Petroleum closures require vapor check valves in the vapor-gathering lines to prevent the vapor from discharging back to the atmosphere when the loading assembly is withdrawn.

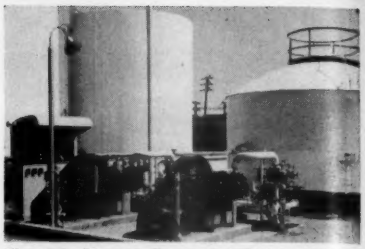

Fig. 14. Vapor disposal unit to refinery fuel gas system showing gas blanketed vapor holder compressors, and instrumentation.

Vapor Disposal

Three general methods are being used to comply with the vapor disposal requirements of Rule 61 — burning the vapor for fuel, absorbing the vapor in package absorption units and venting the vapor to existing tank farm vapor recovery systems.

The first method (Fig. 14), utilizing the vapors directly as supplementary fuel, must use gas blanketing to avoid explosive mixtures. The vapors pass through a drip pot or in some designs into a small vapor holder before being compressed to the pressure of the refinery fuel system. Condensate recovered at the drip pot is normally drained to the gasoline slop tanks.

The second method (Fig. 15 and 16), utilizes a "Vapor Saver", a package absorption unit developed by the Superior Tank and Construction Company, and consisting of a vapor sphere, saturator, absorber, compressor, pumps and instrumentation. This unit can be adapted to fit any size operation at any desired loading location since it uses the gasoline product as the absorbent. It is most useful at locations which are at some distance from existing vapor recovery or fuel gas systems. Vapors displaced at the loading rack are passed through the saturator countercurrent to gasoline pumped from storage, being enriched in the process by stripping the gasoline of its lighter components, and are then accumulated in a vapor sphere equipped with a flexible diaphragm.

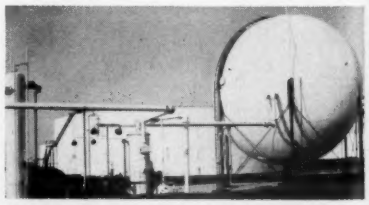

Fig. 15. Close-up view of a large capacity vapor saver absorption unit showing vapor sphere, saturator absorber, compressor, pumps and piping.

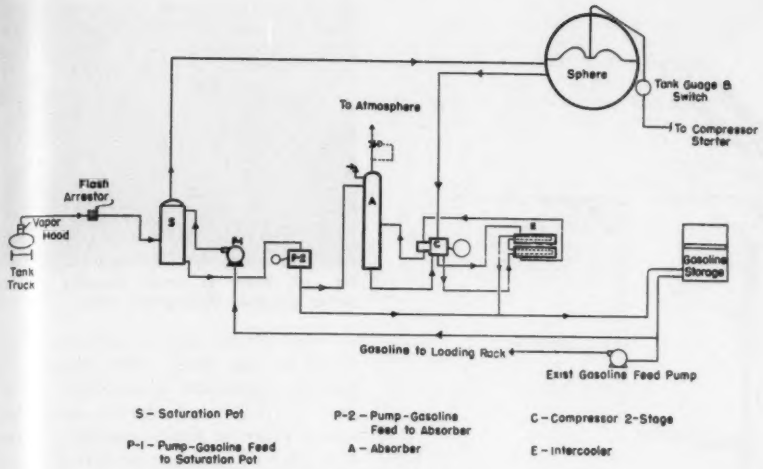

Fig. 16. Schematic flow diagram of a vapor saver unit used for recovery of loading rack vapors at a bulk terminal.

compresses the vapors to approximately 200 psig. and injects them Position of this diaphragm automatically actuates a compressor which into the absorber. Countercurrent flow of stripped gasoline from the saturator or fresh gasoline from storage is used to absorb the hydrocarbon vapors. Gasoline from the absorber bottoms is returned to storage while the tail gases, essentially air, are released to the atmosphere through a back pressure regulator.

In the third method, the displaced vapors go to a gas absorption plant for recovery of condensate while the noncondensible gases are burned as fuel. To utilize such a system only requires a connection into the vapor-gathering line through a regulator valve. Gas blanketing may be used on the vapor lines at the rack to preclude any explosive mixtures being formed.

The efficiencies of these three methods, with complete pickup at the tank vehicle, range from 90 to 100%. Disposal of the vapors by combustion, in a well designed system, is almost 100% effective. Vapor recovery systems are considered to be 100% effective, although, if their design capacities are exceeded at peak loads, efficiencies of less than 100% result. The efficiency of the Superior Vapor Saver Unit has been checked with a mass spectrometer and found to be from 92 to 96% effective on a weight basis.

Conclusions

An intensive development program pursued by the petroleum industry has succeeded in producing equipment capable of collecting and dispersing of the hydrocarbon vapors displaced during the bulk loading of gasoline into tank vehicles. Refinements to the various types of loading arm assemblies have overcome the problems posed by tank settling during loading and liquid drainage from the loading spout after loading, as well as eliminating "open topping". Inasmuch as equipment manufacturers have been involved in the development program, the equipment items comprising a control system are commercially available.

Where the loading into tank vehicles is performed near existing vapor recovery facilities (or gathering lines) absorption plants or fuel gas systems, they can be used to dispose of the vapors. At other locations, such as bulk terminals or bulk plants, where such facilities do not exist, a separate package-type disposal system has been devised. This latter system employs absorption of the displaced vapors in liquid gasoline at about 200 lbs. pressure to recover all but a few per cent of the displaced hydrocarbon vapors. Each of the described types of control equipment has been installed and in operation for nearly a year and each has proven workable and effective. A systematic program of maintenance should guarantee continued usage without excessive costs.

Addition of Rule 61 to the Rules and Regulations of the Los Angeles County Air Pollution Control District made mandatory the installation of control equipment at the larger tank vehicle loading installations at which 85 to 90% of the gasoline gallonage is loaded. Compliance with this rule by the industry has resulted in an estimated reduction of hydrocarbon vapor emissions of about 30 tons daily.

These controls represent investments of approximately three million dollars by the petroleum industry and payouts are estimated at thirty months to five years. Besides recovery of products in some of the control systems, other values have resulted. These include better working conditions for operating personnel, prevention of petty gasoline theft, and in some instances, sales tax refunds. Gasoline losses from spills, overfills and loading arm drainage have also been minimized.

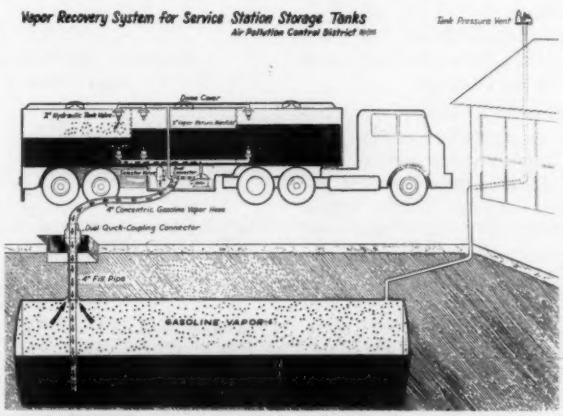

Fig. 17. Schematic drawing of a proposed vapor return system for controlling delivery vapor losses at small bulk plants and service stations.

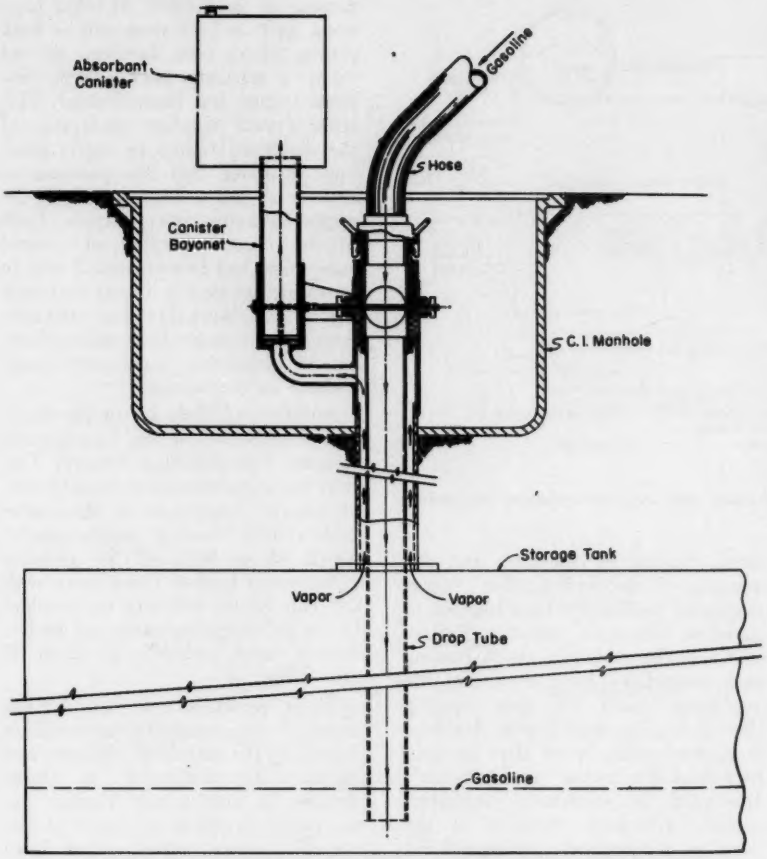

Fig. 18. Schematic drawing of a proposed adsorption system for controlling delivery vapor losses at small bulk plants and service stations.

Further extension of the type of legislation represented by Rule 61 to the smaller bulk plants, service stations, automobile and aircraft fueling is expected. Preliminary design [10] and a working model for a vapor return type control device for such operations has been devised and tested [11] by the District

For retail service station deliveries, two solutions appear feasible. The first is a vapor return system and the second an adsorption system using activated carbon. In the vapor return system (Fig. 17), the displaced vapors are collected in the delivery vehicle and returned to the bulk terminal or refinery for disposal. In the adsorption system (Fig. 18), the activated carbon would require periodic regeneration for recovery of the vapors and re-use of the carbon. Testing performed after the writing of this report shows that the adsorption of concentrated hydrocarbon vapors by activated carbon may not be feasible due to the excessive heat resulting from adsorption.

The same control methods applying

Fig. 19. View of small capacity vapor saver gasoline absorption unit.

to retail service station deliveries also apply to the small bulk plants. In addition, gasoline absorption units, such as the Vapor Saver, could be scaled down to their capacities. (See Fig. 19.) A variation of this absorption system has been proposed in which the vapors from the rack are drawn into an eductor and absorbed in liquid gasoline. This mixture is then piped to the suction of a pump and there mixed for further absorption in the pump with additional gasoline from storage. (See Fig. 20.)

For automobile fueling, the proposed design includes tight fill with a vapor return system in which the displaced vapors are returned to the underground service station tanks from which, eventually, they will be transported to a disposal unit at a bulk terminal.

Control of vapors at aviation fueling facilities may also be solved by a vapor return system but more instrumentation may be necessary as many aircraft are bottom loaded under pressure.

If control of the delivery losses in Los Angeles County at the service

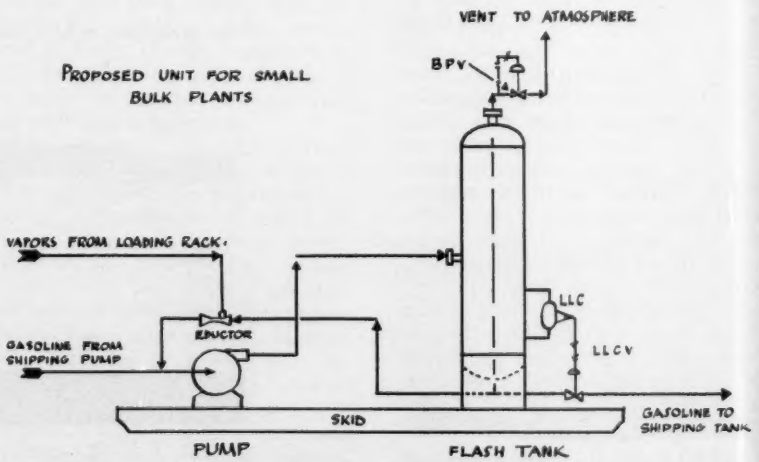

Fig. 20. Schematic flow diagram of a proposed absorption system for controlling loading vapor losses at small bulk plants.

station and automobile can be realized, hydrocarbon vapor losses from this type of operation could be further reduced by about 60 tons/day.

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Nitric Oxide and Nitrogen Dioxide Concentrations Near the Ground at Menlo Park, California*

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Menlo Park, Calif.

The oxides of nitrogen and organic compounds are known to participate in the photochemical reactions which produce the Los Angeles type smog. Because of the great interest in these reactions, a monitoring program was carried out at Stanford Research Institute at Menlo Park, Calif., from Oct. 1956 through Mar. 1957, to determine the nitric oxide and nitrogen dioxide content in the air by the new automatic analyzer [4] for these gases. Wind, temperature, and sunshine records covering most of this period were also made.

The area represented by this sampling is primarily residential. The occupied region is a long and comparatively narrow strip, (a few miles at its widest point) extending in a southeasterly direction from San Francisco to San Jose, 40 mi. away. Two parallel major highways, about a mile apart, and a railroad having frequent commuter trains on weekday mornings and evenings, traverse the axis of the strip.

The sampling station is located between the two highways, about 0.2 to 1.0 mi. distant from the nearest residences, which are all heated by gas. The Institute's heating plant with its 50-ft. stack is 0.2 mi. to the west-southwest. No industries producing other types of air pollution are present in the neighborhood. The nearest heavy industry is a cement plant about 5 mi. northwest of the station. It is presumed that the sources of the nitrogen oxides found in the air are gas or oil fired furnaces and traffic. Some Los Angeles-type smog is present in the area during the autumn and winter, as indicated by lowered visibility, occasional plant damage, and infrequent complaints of eye irritation.

*Presented at the 40th Annual Conference of The Chemical Institute of Canada, Vancouver, B. C., June 3, 4, 5, 1957.

Editor's Note:
It was our intention to publish this paper simultaneously with that by L. H. Rogers "Nitric Oxide and Nitrogen Dioxide in the Los Angeles Atmosphere", which appeared in the August Journal. Unforseen circumstances prevented this. We suggest that the two papers be read and studied together.

Air Analysis. A description of the NO_2-NO recorder has recently appeared [4]. The nitrogen dioxide is absorbed in a modified Griess reagent for nitrite and determined colorimetrically. The nitric oxide in another sample of air is oxidized by permanganate to nitrogen dioxide and the total gas determined separately. Operation of the recorder is essentially trouble free. The permanganate solution is an excellent oxidizing agent for nitric oxide, but it must not be allowed to concentrate appreciably by evaporation, and occasional replacement with fresh solution is necessary. The Griess reagent can be used repeatedly for a month or more before it begins to develop a green color after passing through the charcoal filter. The green color is slowly discharged after adding more coupling reagent, but when it becomes strong there is interference with the recording for a few min. after reversing the direction of the solution. Fresh charcoal will remove the green color and prolong the life of the solution. The charcoal should also be changed when a new solution is made up. The life of the charcoal can be greatly increased by washing it with hot acetic acid and heating to 200-400°C. before use or re-use. Tiny bubbles are slowly released from the reagent and tend to accumulate in the "zero" cell, raising the recorder "zero." These may be removed automatically by allowing a bubble of air at about 20-30 minute intervals, to leak into the line to the cell through a very fine capillary. This bubble will effectively sweep out the cell. No trouble has been experienced in a year's operation of the liquid pumps or the Zenith air pumps. Calibration of the instrument has remained unchanged since the final value was established as reported earlier [4].

Results

Diurnal Records. Fig. 1 gives the detailed trace of nitric oxide and nitrogen dioxide values in pphm. parts of air for Thurs., Dec. 27, 1956. This day was cloudless and nearly free from wind, except for slow air movement between 9:30 a.m. and 4 p.m., which ranged from 0 to 5 mph. and came from the north sector. During the remainder of the day, air movement, if any, was less than 2 mph., and generally originated from the south and south-southeast. The temperature was 34°F. at 3 a.m. on Dec. 27. It reached a minimum

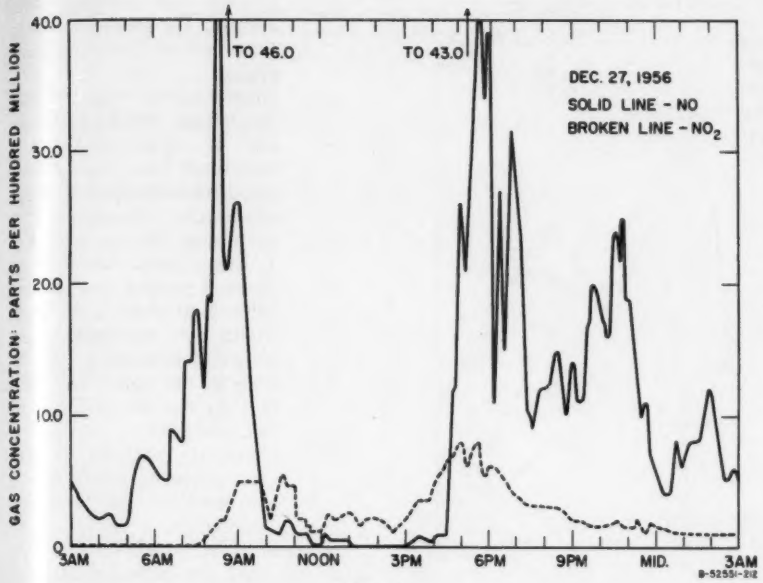

Fig. 1

of 31° at 7 a.m., 50° at 10 a.m., a maximum of 66° at 3 p.m., 50° at 5 p.m., and 34° at 3 a.m. on Dec. 28.

The bimodal curves for the two nitrogen oxides are characteristic of nearly every day of low wind velocity. When there was appreciable wind throughout the day, the concentration of the gases fell to a level so low that a distinct pattern was not often apparent. Even the slow air movement from 9:30 a.m., to 4 p.m., on Dec. 27 was sufficient to lower NO and NO_2 levels considerably below the expected levels for this time of day when there is little or no wind. The maximum values for the two gases recorded in Fig. 1, namely, 46 and 8 pphm., were also recorded on many other days but were not exceeded significantly. The highest NO and NO_2 readings observed at any time were 53 and 15 pphm., respectively. The morning maximum for NO occurred at 8:20 a.m. In the evening (5 to 12 p.m.) the concentration remained high and a number of maxima and minima occurred during this period. The morning maximum for NO_2 was reached later than the NO peak, after the declining NO curve had crossed the increasing NO_2 curve. The NO_2 concentration was greater than the NO between about 10 a.m. and 4 p.m. on clear days. In the evening both curves rose — NO more rapidly than the NO_2. NO and NO_2 values for a single day in Pasadena, Calif., are given elsewhere [4]. The two gases were nearly identical in concentration at a low level during the 8 a.m. peak and a high afternoon peak was not present. Otherwise the curves were generally similar to those in Fig. 1.

Monthly Records. Fig. 2 gives the NO and NO_2 values for Nov. 1956 and Mar. 1957 as hourly average concentrations for each month in pphm. of air — again on days of little or no wind. Each point represents the average for the hour following the time indicated. Fig. 3 gives the average hourly NO data for each of the six months from Oct. 1956 to Mar. 1957, and Fig. 4 gives the corresponding NO_2 data.

The curves are essentially similar to those for the single day shown in Fig. 1. It should be noted that the ordinate scales in Fig. 2 and 3 are half that of Fig. 1, and the scale in Fig. 4 is only one-fifth of Fig. 1. Fig. 2 shows the striking contrast between the diurnal curves for NO and NO_2, which is apparent whether the monthly gas levels are high or low. The NO predominates over the NO_2 at night and in the early morning. The reverse is true during the day from about 9-10 a.m. and to 4-6 p.m. Also, the average level of NO cencentrations is much greater than the NO_2 average level. This suggests that NO is the primary compound produced at the source, presumably a union of nitrogen and oxygen taking place during the combustion processes as mentioned earlier. The NO_2 is produced later either by photochemical reactions in the atmosphere or by slow combination of NO with oxygen.

In Fig. 3, a high degree of similarity is apparent in the nitric oxide curves of the different months, particularly during the mornings. In fact, the curves for Nov., Dec. and Jan. are nearly identical. If the values for Feb. were to be multiplied by 2, the resulting curve would also be nearly identical with those of the three preceding months. Oct. and Mar. have their maxima an hour earlier in the morning, also later in the evening owing to longer days.

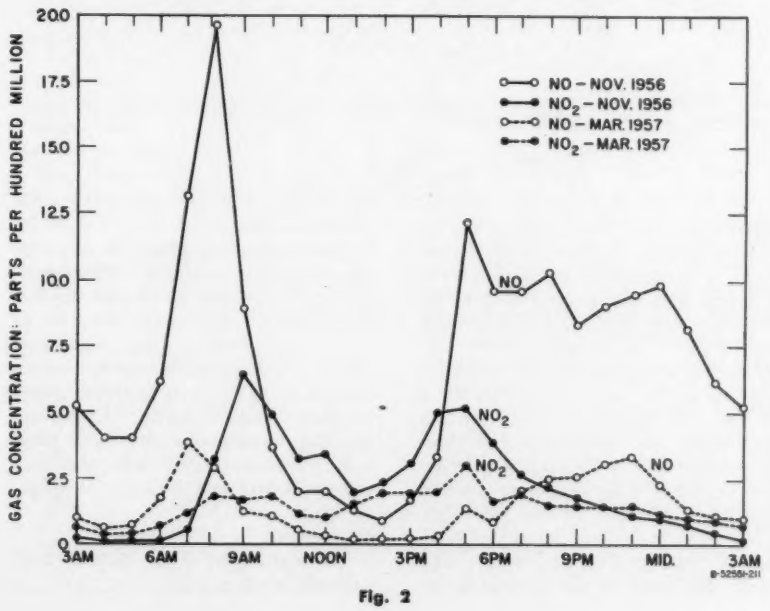

Fig. 2

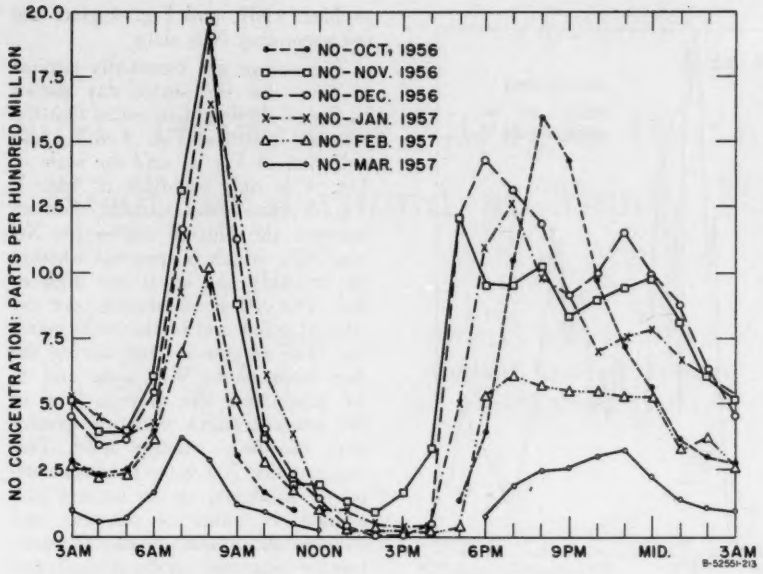

Fig. 3

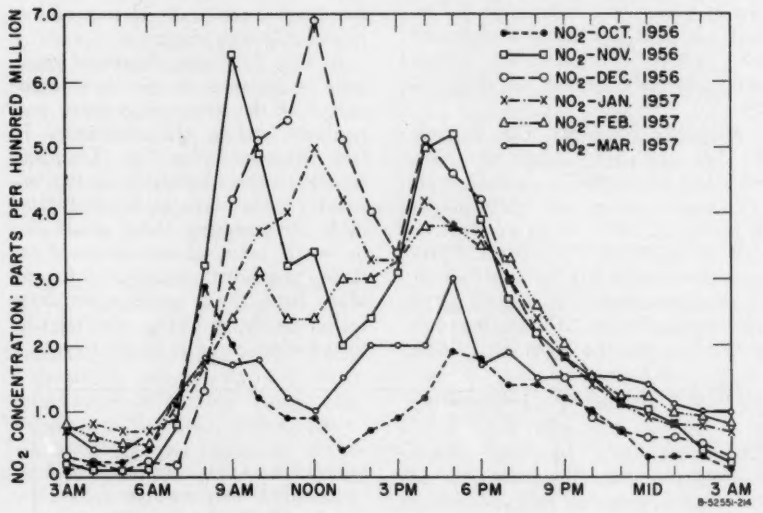

Fig. 4

In Fig. 4 the nitrogen dioxide curves for Nov., Dec., Jan., and Feb. run very close together from 3 p.m. until 7 p.m., with a maximum at 4-5 p.m. and a minimum at 4-5 a.m. The curves for Oct. and Mar. remain low from 3 to 9 p.m. before approaching the other curves closely for the rest of the night. From 8 a.m. to 3 p.m. all the curves show another maximum and minimum, but there is a large spread between the different months. The maximum occurs just after 12 noon in Dec. and Jan. after 10 a.m. in Feb., 9 a.m. in Nov., and 8 a.m. in Oct. and Mar. Similarly, the time of the minimum extends from 3 p.m. back to noon for these months.

The monitoring program was continued in Apr. and May. The results are not reported in detail at this time because they were too low to be of much interest. The maximum values of NO_2 and NO in April were 6 and 16 pphm., respectively, and in May, 5 and 9 pphm. The corresponding averages of the daily peak concentrations were 2.8 and 4.5 pphm. in Apr. and 2.7 and 2.0 pphm. in May.

Discussion

The variations of the data in Fig. 1-4 are due to:

(1). Diurnal and monthly variations in the amount of these gases emitted into the atmosphere.

(2). Meteorological conditions controlling dispersion. Periods of appreciable wind movement have been eliminated from consideration because the atmosphere is swept clear of contamination at these times. Attention is directed toward periods of calms and those with very slight air movement — together representing 80 to 90% of the time from Nov. to Feb. and 60 to 70% in Oct. and Mar.

(3). Chemical reactions in the atmosphere by which NO is converted into NO_2 or other compounds.

Sources of NO_2 and NO. It seems probable that the principal sources of oxides of nitrogen in the Menlo Park area are home furnaces, industrial heating plants, and traffic, as indicated in the foregoing. In view of the peak concentrations recorded in the morning and evening, more or less coincident with traffic peaks, it was thought that traffic might be an especially important contributor, particularly at these times.

Table I gives the hourly traffic count on Sun. and Mon., July 15 and 16, 1956, on the two large parallel highways passing through Menlo Park. The total count on these roads, plus the cross traffic on one of them, not included in Table I, was nearly 100,000 vehicles in 16 hr. There may be an additional 20,000 in the city. The volume of traffic increases about 20% from a minimum in Jan. to a maximum in July and Aug.

It is evident that the count on Monday is highest in the morning between 7 and 9 a.m. and in the afternoon between 4 and 6 p.m. when the peaks of nitrogen oxides occur. However, the count remains high between 9 a.m. and 4 p.m., when minimum concentrations of nitrogen oxides occur. On Sun. mornings the count and oxides of nitrogen are both low. Data for the latter are given in Table II, which indicates that the concentration of nitrogen oxides is only about one-third as high on Sun. as on week-day mornings. There is a great reduction in the level of nitrogen oxides in Oct., Feb., and Mar. as compared with Nov., Dec. and Jan. This reduction

TABLE I
Diurnal Traffic Count on the Two Arterial Highways in Menlo Park For Sunday And Monday, July 15-16, 1956

	Thousand Vehicles/Hr.			
	Bayshore Freeway US 101 By.		El Camino US 101	
Time	July 15	July 16	July 15	July 16
6 a.m.	0.54	1.93	0.15	0.56
7	0.74	3.35	0.38	2.47
8	1.19	2.57	0.51	2.53
9	1.92	2.09	1.00	1.97
10	2.54	2.55	1.54	2.69
11	2.83	1.57	1.63	2.47
12	2.94	1.84	2.18	2.90
1 p.m.	3.05	1.87	2.28	2.66
2	2.49	2.33	2.59	2.82
3	3.18	2.52	2.87	3.04
4	3.09	3.57	2.86	3.71
5	2.92	3.37	2.99	4.10
6	2.79	2.25	2.37	1.71
7	2.95	1.54	2.05	1.73
8	2.72	1.25	2.36	1.77
9	2.46	1.10	2.28	1.71
TOTAL	38.36	35.70	30.01	38.94

is greater still in the summer, when traffic is greatest, suggesting that there is at least one other important contributor during the winter.

Space heating, which is dependent on the temperature of the atmosphere, wind velocity, and the habits of the population, could be this contributor. This source, as indicated by the quantity of natural gas consumed in the area, appears to vary in a manner similar to the diurnal and monthly variations observed in the concentrations of nitrogen oxides (Tables III and IV). Rate of gas consumption is greatest in the morning between 7 and 9 a.m. and from early evening until midnight. It is least during the early afternoon and between midnight and 6 a.m. These are the periods of maxima and minima of nitrogen oxides.

Fig. 5 gives the hourly rates of gas supply to the city of Palo Alto from Dec. 31, 1956 to Jan. 2, 1957. This municipality receives the gas by meter from Pacific Gas and Electric Company and distributes it to its consumers. There is no storage capacity in the system except for that in the distribution pipes where the pressure may vary from 5 to 15 lb. There is a general similarity between the gas supply curves and the measured concentrations of $NO_2 + NO$ in the atmosphere, except for Jan. 1, when a presumed large consumption of gas during the preceding night was not replaced in the mains until morning.

Table IV gives the actual and relative monthly average gas consumption rates in Menlo Park and Palo Alto in comparison with the relative monthly average concentrations of $NO_2 + NO$ during periods of little or no wind. The corresponding values appear to be similar, being greatest in the coldest months. The monthly average of the daily minimum temperatures was 34 to 36°F. in Nov., Dec., and Jan., and 44 to 45°F. in Feb. and Mar. The corresponding values of the maximum fell from 65 to 52°F. between Nov., and Jan., then rose to 61°F. in Mar.

The relative monthly gas consumption rates in both Palo Alto and Menlo Park, based on Dec. as unity, are plotted in Fig. 6 and show approximate agreement with the corressponding relative monthly $NO_2 + NO$ values though in Feb. and Mar. the latter fall off more rapidly than the gas consumption. This agreement suggests the likely existence of a cause and effect relationship between these variables. The discrepancies between the ratios can probably be explained by the prevalence of more wind in Feb. and Mar. which presumably would increase the relative gas consumption for those months and at the same time reduce the nitrogen oxide levels. The almost complete absence of wind in Nov. and Dec., particularly at night, resulted in persistent fairly high level recordings nearly every night, whereas in Mar., such recordings were much less frequent.

An estimate of the contribution of nitrogen oxide, from both traffic and space heating with natural gas, is presented in Table V. If there were 120,000 vehicles in 16 hr., each travelling 1.5 mi. in the 3 mi.^{2} area of Menlo Park. they would consume about 4 gal. of gasoline/mi.^{2}/min. Similarly, average winter consumption of natural gas (Table IV) would reach about 1200 cfm./mi.^{2}/min. in Menlo Park. Under average urban driving conditions, the data of Elliott, *et al*[1] and Stanford Research Institute[2] indicate the production of about 0.8 to 1.5 cu. ft.[3] of nitrogen dioxide per gal. of gasoline. Further, nitrogen dioxide production from natural gas[3] varies over a wide range from 0.1 to 0.6 vol.% of the gas burned. It appears that on the average the contributions of nitrogen oxides from traffic and winter space heating to the atmosphere of Menlo Park are nearly identical, totaling about 0.3 pphm./min. in the lower 100 ft. Peak contributions may be 3 times the average so that amounts up

TABLE II
Average NO_2 And NO Concentrations On Sunday Mornings As Compared With Weekday Mornings Under Similar Meterological Conditions

	Sundays			Weekdays		
Time	No.	NO_2, pphm.	NO, pphm.	No.	NO_2, pphm.	NO, pphm.
6- 7 a.m.	15	0.2	3.4	92	0.5	4.2
7- 8	15	0.4	3.8	96	0.9	8.9
8- 9	15	1.1	4.7	96	2.1	13.1
9-10	15	2.4	3.8	87	3.5	7.7
10-11	15	2.5	2.1	68	3.6	3.6

TABLE III
Diurnal Demand For Natural Gas In Northern California At Mean Temperature 29.1°F. (1950-51)

	Demand, million ft.^{3}/hr.	
Hr.	AM	PM
12-1	38	68
1-2	37	63
2-3	38	59
3-4	39	58
4-5	41	62
5-6	50	70
6-7	64	73
7-8	80	69
8-9	86	62
9-10	84	55
10-11	79	48
11-12	74	42

TABLE IV

Monthly Consumption Of Natural Gas in Menlo Park And Palo Alto as Compared With the Relative Concentrations of Nitrogen Oxides

Date 1956-57	Gas consumption, million ft.³/day			Relative Average	
	Menlo Park	Palo Alto		Gas	NO_2+NO
	av.	av.	max.	Consumption	Conc.
Sept. 15 - Oct. 15	1.76			0.36	
Oct. 1 - Oct. 31		5.30	9.12	0.52	0.46
Oct. 15 - Nov. 15	3.19			0.65	
Nov. 1 - Nov. 30		8.00	10.39	0.78	0.97
Nov. 15 - Dec. 15	4.52			0.92	
Dec. 1 - Dec. 31		10.25	12.77	1.00	1.00
Dec. 15 - Jan. 15	5.20			1.06	
Jan. 1 - Jan. 31		11.25	14.35	1.10	1.01
Jan. 15 - Feb. 14	5.43			1.10	
Feb. 1 - Feb. 28		8.28	11.89	0.81	0.72
Feb. 14 - Mar. 15	3.71			0.76	
Mar. 1 - Mar. 31		7.28	9.49	0.71	0.40
Mar. 15 - Apr. 15	3.04			0.62	
Apr. 1 - Apr. 30		5.77	8.55	0.57	

Area Palo Alto 10.6 mi.²
Area Menlo Park 3.2 mi.²

TABLE V

Estimated Winter Contribution of Nitrogen Oxides, as Nitrogen Dioxide, to the Lower Atmosphere of Menlo Park Due to Traffic and Space Heating by Natural Gas

	Gasoline	Natural Gas
Consumption/mi.²	4 gal./min.	1200 cfm.
NO_2 evolved range /mi.²: average	3 to 6 cfm. [1, 3] 4.5 cfm.	1.2 to 7.2 cfm. [3] 4.2 cfm.
NO_2/min. to lower 100 ft. of atmos. (2.8×10^9 ft.³)	0.16 pphm.	0.15 pphm.

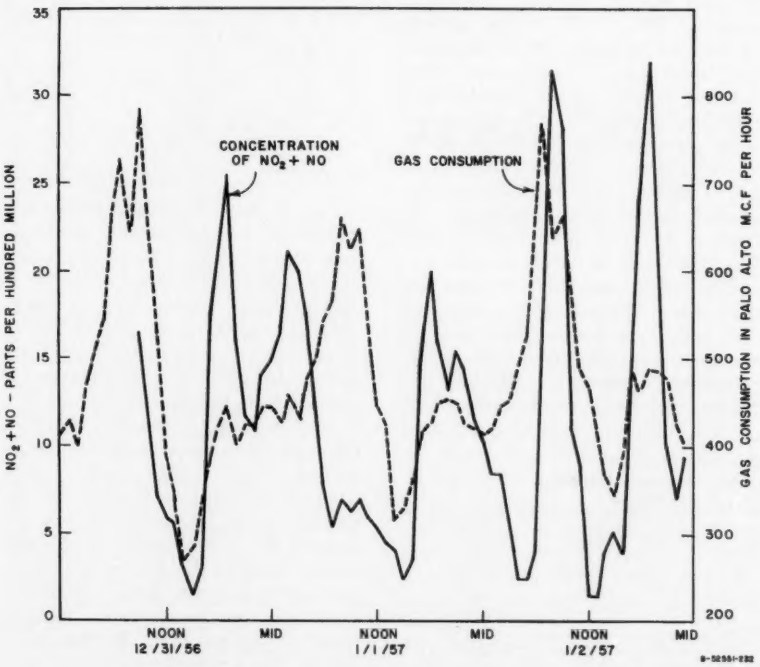

Fig. 5

to about 1 pphm/min. would be expected at times. With very slow wind movement and strong nocturnal and early morning inversions, large accumulations near the ground would be possible. Peak concentrations of 50 pphm. due solely to these two sources do not seem unreasonable.

It may be noted that the combustion products from space heating are distributed more or less uniformly over the area, whereas those from traffic originate largely on the two highways which are respectively one half and one mi. distant from the sampling station at their nearest point. This may explain the better concordance of the nitrogen oxide pattern with the space heating than with the traffic pattern.

Wind Direction and Velocity. From a casual inspection of the record, it is apparent that wind velocity is the primary meterological factor involved in accumulating the oxides of nitrogen. On days of considerable wind, 5 to 10 mph. or more, no more than traces of the two gases were registered at any time. This was also generally true with lower wind velocities, 2 to 5 mph., though at times moderate registrations occurred under these conditions. It was only in periods of virtual calm that consistent recordings were obtained at the highest levels of concentration. Since the anemometer required a wind speed of 1.5 mph. to initiate movement, a "calm" might represent air movement up to about 2 mph. At these very low velocities, wind direction seemed to have little effect on the recordings.

It has already been mentioned that the "built-up" area on the San Francisco Penisula is long and narrow. Wind from the sector 280 to 320° would travel along the axis from the northwest, while the sector 120 to 150° would cover the axis from the opposite direction. In other directions the residential areas do not extend more than 1 to 3 mi. from the sampling site.

The low concentrations between 10 a.m. and 4 p.m. on Dec. 27 (Fig. 1) occurred with velocities up to 4-5 mph. and from directions from north to east. With wind movement of 2-3 mph. during the rest of the day, the recorded higher concentrations occurred with directions of 330 or 150 to 160°. An interesting observation was made during Feb. 6-7. With a slow drift of air from 330° at 11 to 11:30 p.m., the NO_2 and NO registered 3 and 8 pphm. respectively.

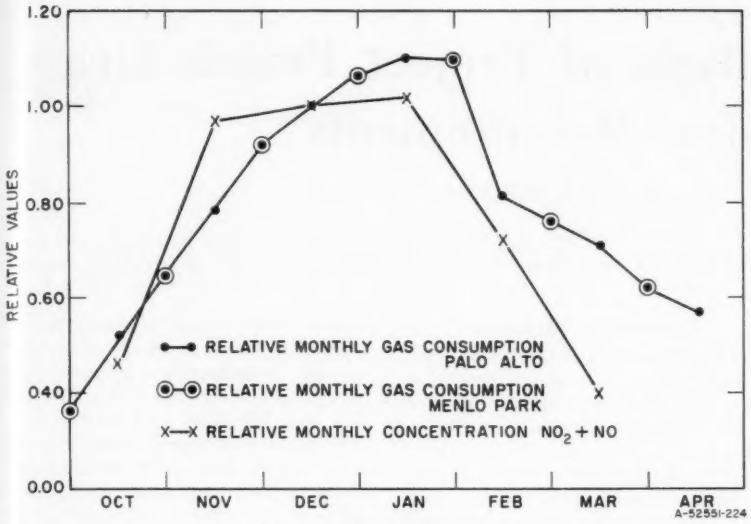

Fig. 6

At 11:30 p.m. a somewhat turbulent wind started from the south (180°) at 3-5 mph. It continued until 12:00, then changed to 125° at 2-4 mph. until 12:40 a.m., before quieting at 140°. The NO_2 and NO curves fell to zero between 11:40 and 11:50 p.m., where they remained until 12:10 a.m. At 12:20 a.m. they again registered 5 and 8 pphm. Considering the lag of about 10 min. in the recording, it appears that the gust of wind from the south removed the gas completely, but that it returned immediately when the wind changed to the southeast even though the wind speed fell only slightly.

Other Factors. Table VI illustrates several conditions that affect the recordings of the gases. On Jan. 1, unusually high concentrations were noted after midnight until 6 a.m., followed by the absence of the 8 a.m. peak. This condition occurred only on Sun. and holiday mornings. The high concentrations usually did not persist after 2 a.m. on Sun., but on Nov. 25, Dec. 2, 29, and 30; Jan. 1, and Feb. 22 they were present until 4 to 6 a.m. On Dec. 25 they were high until 2 a.m., then fell off owing to wind. The record was lost for Dec. 31. Presumably a considerable part of the population retires late and arises late on these days, with consequent modification of the space heating and traffic schedule. Comparison of Jan. 1 and 2 shows this clearly.

Jan. 2, like Dec. 27 in Fig. 1, was a clear morning of low wind velocity, 3 mph. until 11 a.m. Wind directions on the two mornings were somewhat different, Dec. 27 beng constant at 130 to 160° during most of the period. It is of interest to observe how concordant the nitrogen oxide concentrations appeared to be on the two days in spite of slight differences in wind velocity, larger differences in direction, and a temperature range of 31 to 60°F. on Dec. 27 as compared with 33 to 50°F. on Jan. 2.

The morning of Jan. 5 was overcast with some rain, but the wind speeds were low. The temperature ranged from 40 to 50°F. Nitrogen oxides were quite low, only trace amounts being present before 6 a.m. while the 8 a.m. peak did not exceed 9 pphm.

Low values of the morning peak concentrations on overcast days is a general occurrence. Table VII *(see page 277)* lists the average 8-9 a.m. values on all comparable wind-free days with and without clouds, during Dec., Jan. and Feb. The table also lists the average NO concentration between 6 p.m. and midnight under conditions similar to 8 a.m. data. Concentrations were always higher on comparable days with clear skies. Differences were greater in the morning than in the evening. During the early afternoon, some wind movement generally present and concentrations were so low that the effect of clouds was not apparent.

Summary

A monitoring program for NO_2 and NO in the atmosphere in Menlo

(Continued on page 277)

TABLE VI
Wind Movement and Concentration of Nitrogen Oxides During the Morning Hours on Three Days

	Jan. 1			Jan. 2			Jan. 5		
	Wind			Wind			Wind		
Time, a.m.	Dir.	Vel., mph.	NO_2+NO, pphm.	Dir.	Vel., mph.	NO_2+NO, pphm.	Dir.	Vel., mph.	NO_2+NO, pphm.
12-1	150	<2	15	Var.	<2	10	360 (b)	1-5	1
1-2	160	<2	17	300 (a)	<2	8	170 (a)	<2	1
2-3	200	<2	21(24) (c)	140 (a)	<3	8	Var.	<3	3
3-4	150	<2	20	150	<2	6	150	<3	1
4-5	150	<2	18	150 (a)	<2	2	180	<2	1
5-6	160	<2	12	280 & 130	<2	2	320 (a) & 120	<2	1
6-7	150	<2	8	130	<2	4	150	<2	2
7-8	150	<2	6	100	<2	12	160 (a)	<2	7
8-9	150 (a)	<3	7(8) (c)	100	<2	32(40) (c)	10	2-4	6(9) (c)
9-10	150 (a) & 330	<2	7	20 (a)	<2	28	360 (b)	2-5	1
10-11	10 (a)	<3	7	60 (b) & 330	<3	11	10 (b) & 270	1-3 & <2	0
11-12	Var.	<2	6	330 (b)	2-5	9	210 (a)	<2 & 1-3	1
Weather:		Clear			Nearly clear			Raining	
Min.-max. temp:		33-52°F.			33-50°F.			40-50°F.	

a Slight turbulence
b Appreciable turbulence
c Peak concentration

Preliminary Analysis of Project Prairie Grass Diffusion Measurements*†

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Introduction

During the summer of 1956, an extensive empirical investigation of atmospheric diffusion was conducted at a field site near O'Neill, Nebraska under sponsorship of the Air Force Cambridge Research Center (Project Prairie Grass). The field site was carefully selected to provide level terrain, uniform vegetation cover (maintained at an average height of about 6 cm. by mowing), and practically complete freedom from large roughness elements. Objectives of the observational program included determination of the rate of diffusion of a gas tracer, emitted from a continuous point source near ground level, as a function of meteorological parameters. As a participant in Project Prairie Grass, the Massachusetts Institute of Technology made measurements of average gas concentrations over a range of 800 m. and of certain meteorological parameters related to the structure of turbulence. The experiments were conducted in a wide variety of weather conditions (wind speed, cloud cover, thermal stratification, *etc.*). A preliminary analysis has been made of the diffusion measurements and of some of the meteorological observations. This paper briefly describes the conduct of the diffusion experiments; summarizes basic features of plume structure and behavior thus observed; and, discusses empirical relations between diffusion and 2 simple meteorological parameters—the standard deviation of azimuth wind direction and the stability ratio.

* Presented at the 50th Annual Meeting of the Air Pollution Control Association held in St. Louis, Mo., June 2-6, 1957.

† Research sponsored by the Geophysics Research Directorate, Air Force Cambridge Research Center, under Contract No. AF 19(604)-1058.

a. In 6 experiments, the tracer was released at a height of 1.5 m.; no significant changes were noted in the measured concentrations as a result of this adjustment.

Experimental Techniques

The diffusion experiments involved determinations of average concentration at selected points downwind from a point source of sulfur-dioxide gas operated continuously for periods of 10 min. Generation of the tracer may be briefly described as follows: Liquid sulfur dioxide from an inverted 150 lb. cylinder was vaporized in a specially-constructed chamber immersed in a large tank of water, the water temperature being maintained at about 50°C. After vaporization, the gas passed through a pressure regulator and a large ironcase meter which registered the total output. The tracer was then conducted through a 50 m. length of 2 in. plastic pipe and released horizontally at a height of 46 cm. above the ground[a]. Rate of emission was maintained constant during the release period and was adjustable to a maximum value of about 100 g./sec. The maximum rate of emission was used during experiments conducted in conditions of thermal instability and a source strength of about 45 g./sec. was used at night in the presence of temperature inversions.

Average gas concentrations were determined at 545 points located within a semicircle of radius 800 m. centered on the release point for the sulfur dioxide. The baseline of the network was oriented along a true east-west line to take advantage of prevailing southerly winds. Midget impingers were mounted at a height of 1.5 m. along 5 concentric semicircular arcs located at travel distances of 50, 100, 200, 400, and 800 m. from the source. An angular separation of 2° was used between impingers at the 4 inner arcs and a separation of 1° was used at 800 m. Average gas concentrations were also determined at 54 points within a limited vertical sampling network located at 100 m. Midget impingers were mounted on 6 towers symmetrically positioned with respect to the center line of the horizontal network and spaced at 14° intervals along the 100 m. arc. Concentration measurements were made at heights of 0.5, 1.0, 1.5, 2.5, 4.5, 7.5, 10.5, 13.5, and 17.5 m. Eleven vacuum pumps suitably located along the arcs of the sampling network provided aspiration for the impingers. When the network was in operation, air entered the impingers through short sections of capillary tubing and was bubbled through 10 ml. of dilute (slightly acidified) hydrogen-peroxide solution. Sulfur dioxide present in the air samples reacted with the hydrogen peroxide to form sulfuric acid. Average gas concentrations were determined by laboratory measurements of the conductance of the aspirated solutions, using a conductivity cell and a Wheatstone bridge. This technique permits accurate determination of concentrations as low as 0.01 ppm. An aspiration rate of 1.0 *l.*/min. was used at 50 m. and 100 m.; a rate of 1.5 *l.*/min. was used at the other travel distances to compensate, in part, for the decrease in concentration with distance. During the diffusion experiments, operation of the sampling networks commenced immediately prior to the start of the gas release and continued until the tracer had cleared the 800 m. arc; this usually required a period of 2 to 5 min. after the end of the gas release. Laboratory tests indicate collection efficiencies in excess of 97% for all Prairie Grass diffusion experiments. Similar experimental techniques were previously employed in diffusion studies at Round Hill[1, 2]. Detailed accounts of the experimental techniques used during Project Prairie Grass will be found in a collection of papers to be published by the Air Force Cambridge Research Center.

Basic Features of Plume Structure

Seventy gas releases were made during Project Prairie Grass; 34 of these were made during the daytime when the air near the ground was

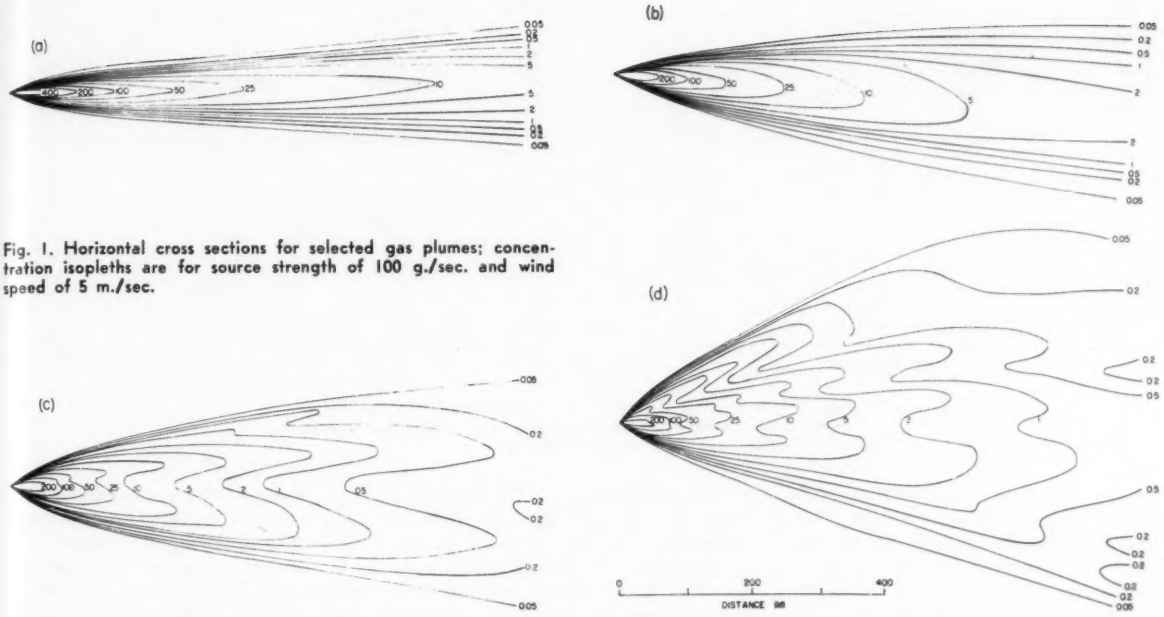


Fig. 1. Horizontal cross sections for selected gas plumes; concentration isopleths are for source strength of 100 g./sec. and wind speed of 5 m./sec.

thermally unstable, and the remainder were made at night in the presence of temperature inversions. Classification of the releases on a daytime-nighttime basis is thus equivalent to classification in terms of unstable or stable thermal stratification. These terms are used interchangeably in the discussion that follows. Nine of the nighttime gas releases are not considered in this paper because of excessive vertical stratification of the plume associated with light, variable winds and strong temperature inverisons. Concentration data and meteorological observations for a small number of additional releases are incomplete. The vertical sampling network at 100 m. was in operation during 57 diffusion experiments.

Four gas releases have been selected to illustrate basic features of plume structure; weather conditions during these releases are summarized in Table I. Concentration isopleths for horizontal cross sections of the selected plumes are presented in Fig. 1; concentrations are expressed in terms of a source strength of 100 g./sec. and a wind speed of 5 m./sec. Fig. 1(a) shows a narrow, symmetrical plume characteristic of stable thermal stratification. Fig. 1(b) shows an exceptionally narrow, symmetrical daytime plume. Fig. 1(c) shows a plume in which the shape of the concentration profile exhibits a marked change with increasing travel distance. Fig. 1(d) shows a wide, irregular plume characteristic of strong midday convection. Vertical cross sections for the 4 sample releases at a travel distance of 100 m. are presented in Fig. 2. Vertical concentration profiles for the Prairie Grass experiments are discussed in a later section of this paper. Horizontal concentration profiles at 3 travel distances and frequency distributions of azimuth wind direction for the selected releases appear in Fig. 3. The profiles were obtained by expressing concentrations at individual sampling stations along a given arc as percentages of the sum of all concentrations for the arc; the area beneath the concentration profile is thus invariant with distance. Also, daytime percentages at each travel distance were smoothed by a weighted 3-term moving average; nighttime data are unsmoothed. Frequency distributions of azimuth wind direction are based on 10 min. samples; for the source vane, the sampling period corresponds with the duration of the gas release; for the 450 m. vane, the start of the sampling period corresponds approximately with the arrival of the gas plume.

There are several characteristic features of plume structure evident in the Prairie Grass diffusion measurements and, also, in the Round Hill experiments previously mentioned. Due to enhanced dilution at the edges of the time-mean plume, there is a fairly regular decrease in angular plume width, and a consequent increase in the peakedness of the horizontal concentration profile, with travel distance. There is a general correspondence between horizontal concentration profiles at short travel distances and the frequency distribution of azimuth wind direction measured close to the source. Over travel distances of the order of 1 km., the plume appears to be a composite of elementary gas filaments that have traveled downwind from the source along lines of constant azimuth bearing. Recent experiments in England show close agreement between vertical concentration profiles at a distance of 500 m. from an elevated source and frequency distributions of elevation angle[3]. These results have been interpreted as indicating a scale of turbulence for which the Lagrangian correlation coefficient is approximately unity. Significant departures from this simple pattern of plume structure are noted in some of the Prairie Grass experiments. In a few instances, the departure is evidenced by a curvature of the plume axis with no significant alteration in the general appearance of the horizontal concentration profile with increasing travel distance. On other occasions, as shown in Fig. 3(c), the shape of the concentration profile changes greatly over a travel distance of a few hundred meters. These inhomogeneities are in part explained by spatial variations in the frequency distributions of azimuth wind direction.

For simplicity, it is usually assumed in theoretical developments that horizontal and vertical concen-

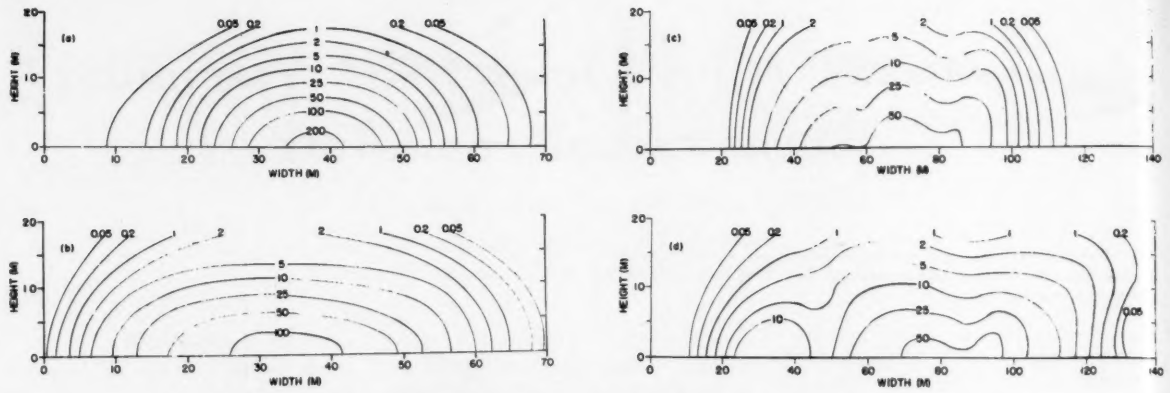


Fig. 2. Vertical cross sections at travel distance of 100 m. for selected gas plumes; concentration isopleths are for source strength of 100 g./sec. and wind speed of 5 m./sec.

tration profiles are distributed according to the normal law of errors. Investigation of the Prairie Grass profiles for horizontal concentration shows that the assumption holds in 17 of the nighttime gas releases; only 2 of the daytime gas releases exhibited horizontal concentration profiles that were approximately normally distributed. Investigation of the form of the vertical concentration profiles is not completed.

Statistical summaries of vertical concentration profile data are presented in Tables II, III. Entries in the tables show the frequency of occurrence of representative normalized concentrations at each sampling height at a travel distance of 100 m. For each gas release, the concentrations at individual towers were normalized with respect to the concentration at the lowest sampling height (0.5 m.); the results at each sampling height were then averaged. At the lowest sampling heights, the diurnal variation in the vertical gradient of concentration is very small. Median values at heights of 1.0 and 1.5 m. fall within the same class intervals for both daytime and nighttime gas releases. At higher levels, the diurnal variation is more pronounced. According to the median values, the average height of the plume is about 12.5 m. for the daytime releases and about 8.0 m. for the nighttime releases[b]. The plume height at 100 m. exceeded 17.5 m. in only 5 (daytime) cases.

b. Plume height and plume width throughout the paper are defined in terms of 1/10 peak concentration: in this case, peak concentration is assumed to occur at a height of 0.5 m.

The relationship between plume width and plume height at a travel distance of 100 m. is shown in Fig. 4. Estimates of plume height were obtained by reference to vertical cross sections based on data from the combined horizontal and vertical sampling networks. The 5 cases in which the plume height exceeded 17.5 m. are not included. The results show that plume height and plume width vary in the same sense, but that increases in plume height occur at a much slower rate than increases in plume width. This is probably a consequence of the suppressive effect of the earth's surface on vertical air motion. The ratio between plume width and plume height thus increases with plume width. Average values of this ratio are 5.6 for the daytime gas releases and 3.9 for the nighttime releases.

Decrease of Concentration with Travel Distance

The decrease in concentration with travel distance is conveniently expressed in terms of a simple power law of the form

$$\chi \propto x^{-b},$$

where χ is the concentration, x is the travel distance, and b is a constant. Peak concentrations and integrated-crosswind concentrations from Project Prairie Grass have been fitted to this type of power law, and values of the exponent b determined for 4 intervals of travel distance (50-100 m., 100-200 m., 200-400 m., and 400-800 m.). Results of this calculation for the daytime gas releases are presented in Table IV. Median values of b for peak concentration increase from 1.85 to 2.35 over the range of travel distance considered. Median values of b for integrated-crosswind concentration increase similarly from 0.85 to 1.55 over the same range. For the nighttime gas releases (Table V), median values of b for peak concentration increase from 1.47 to 1.57 over the first 2 distance intervals and decrease to 1.47 in the interval from 400-800 m. Median values of b for integrated-crosswind concentration remain nearly constant with distance, except for an initial increase from 0.67 to 0.82 over the first 2 distance intervals. It should be emphasized, however, that changes in b with distance show a rather complicated behavior for individual gas releases and significant departures from the general pattern outlined above frequently occur.

Values for b in Tables IV, V are based on measurements made at a height of 1.5 m. and are not necessarily representative of changes in concentration that occur along the plume axis. According to the data in Tables II, III the ratio between the concentration at a height of 1.5 m. and that at 0.5 m. is about 0.92 at a travel distance of 100 m. A somewhat smaller ratio would be expected at shorter travel distances, while at greater travel distances the ratio would be expected to approach unity. Thus, for axial concentration, it is necessary to increase values for b in Tables IV, V that refer to the first 2 distance intervals: b values for the other distance intervals remain unchanged. If the ratio between the concentration at a height of 1.5 m. and axial concentration is assumed to be 0.92 at a travel distance of 100 m., all b values for the 100-200 m. interval of Tables IV, V are increased by 0.12. An increase of 2 or 3 times this amount is indicated for values of

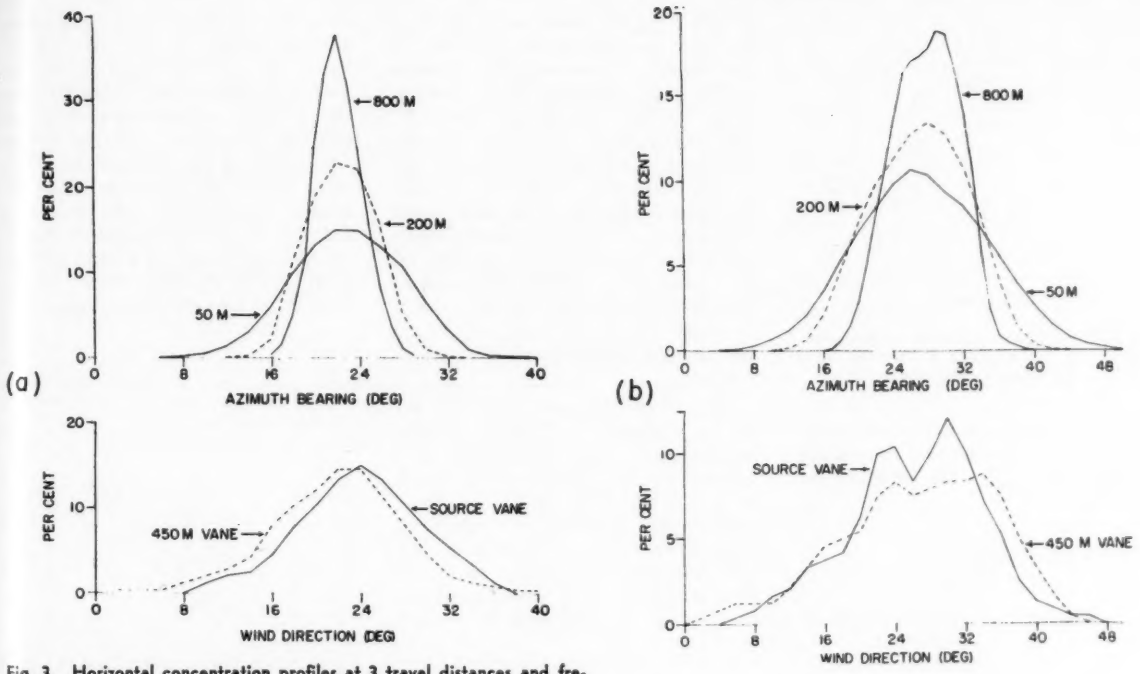
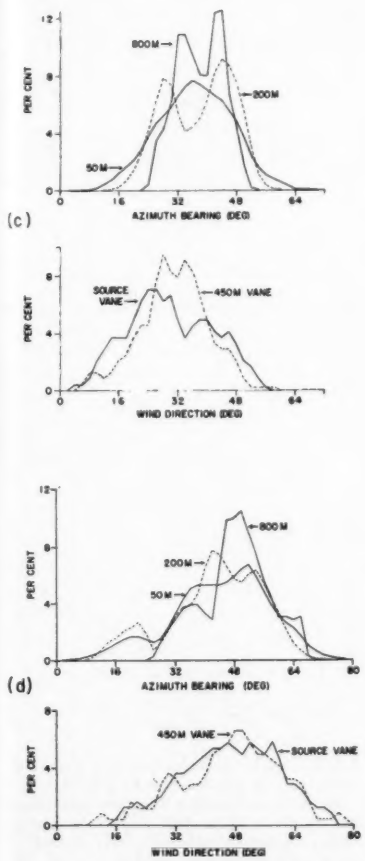


Fig. 3. Horizontal concentration profiles at 3 travel distances and frequency distributions of azimuth wind direction for selected gas releases.



b in the 50-100 m. interval. On the basis of these rough corrections, median values of b for axial peak concentration and integrated-crosswind concentration increase with distance during the daytime gas releases; similar values of b for the nighttime releases show a regular decrease with travel distance. From this preliminary and, as yet, incomplete study of the decrease in concentration with distance, it appears that a simple power law may be valid in conditions of approximately neutral thermal stratification. For other stratifications, particularly in the case of thermal instability, a simple power law becomes increasingly less valid.

It is evident that the exponent b varies not only with travel distance from the source but must also vary with distance from the plume axis. The crossplume variation in b is illustrated in Fig. V. Using the narrow nighttime plume of Fig. 1(a) as a basis, values of b were computed over 2 distance intervals for concentrations measured along lines of constant azimuth bearing from the source. As expected, the results show that the rate of dilution is a minimum on the plume axis and increases sharply at the edges of the plume.

Prediction of Diffusion by Simple Meteorological Parameters

Analysis of diffusion measurements previously obtained for travel distances of 50, 100, and 200 m. shows that basic features of plume structure are highly correlated with fluctuations in azimuth wind direction and with thermal stratification[2, 4]. Fluctuations in azimuth wind direction have also been used as an index of horizontal gustiness and to predict ground-level concentrations for emission from a tall stack[5, 6]. In an initial investigation of empirical relations between Prairie Grass diffusion measurements and various meteorological parameters, basic features of plume structure have been

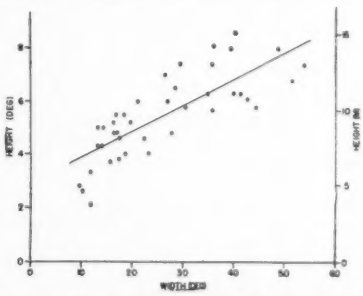


Fig. 4. Scatter diagram of plume height versus plume width at travel distance of 100 m.; open circles are for nighttime gas releases and filled circles are for daytime gas releases.

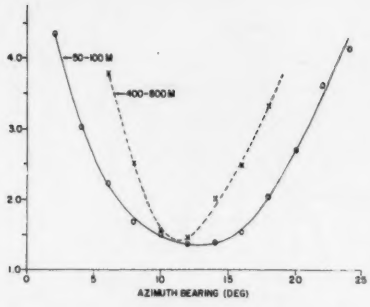


Fig. 5. Crossplume variation in power-law exponent b for 2 distance intervals; data based on gas plume in Fig. 1(a).

correlated with the standard deviation of azimuth wind direction σ_A and the stability ratio *SR*. The latter is defined by

$$SR = \frac{T_{4m} - T_{1m}}{(V_{2m})^2},$$

where T is the temperature in Centigrade, V is the mean wind speed in m./sec., and the subscripts refer to the height of measurement. Values of *SR* were calculated from observations by the Agricultural and Mechanical College of Texas at the Prairie Grass field site. Values for σ_A are arithmetic means of 10 min. standard deviations of azimuth wind direction from the vane located near the source and the vane at 450 m. For simplicity, concentration measurements have been adjusted to a standard source strength of 1 g./sec. and a standard mean wind speed 5 m./sec.

Empirical relations between 4 basic plume characteristics (peak concentration χ_P, integrated-crosswind concentration χ_{CIC}, angular plume width W, power-law exponent b) and the 2 meteorological parameters are summarized in Table VI. Scatter diagrams of the variates are shown in Figs. 6 to 10: solid lines were fitted to the data by the method of least squares. Points to the right of the regression lines in Fig. 8(a), 8(b), 9(b) were not included in the statistical computations. Results from the previous experiments at Round Hill are combined with the Prairie Grass data in Fig. 6(a), 6(b), 7(a), 9(a) and were included in the statistical calculations. (It should be pointed out that the physical characteristics of the site at Round Hill are quite different from those of the Prairie Grass site; the Round Hill

TABLE I

Summary of Weather Conditions During Selected Gas Releases

Release	Time (CST)	Sky	Wind speed (m./sec.)	Temperature gradient
(a)	0100-0110	Clear	5.6	Slight inversion
(b)	1500-1510	Sctrd	9.1	Moderate lapse
(c)	1100-1110	Sctrd	5.8	Moderate lapse
(d)	1400-1410	Brkn	5.9	Strong lapse

TABLE II

Vertical Concentration Profiles at Travel Distance of 100 m. for Daytime Gas Releases

Entries show frequency distributions of concentration at various sampling heights expressed as percentage of concentration at height of 0.5 m.; median values are indicated by asterisks.

Height (m.)	1.0	1.5	2.5	4.5	7.5	10.5	13.5	17.5
%								
110-114			1					
105-109								
100-104	3	2	1	1				
95- 99	13*	2	1		1			
90- 94	7	10*	1	1				
85- 89		8	3		1	1		
80- 84		1	8*	2			1	
75- 79			2					1
70- 74			6	1				
65- 69				3				
60- 64				3	1			
55- 59				2*	1			
50- 54				3		1		
45- 49				3	1			
40- 44				2	2	1	1	
35- 39				2	3	2	1	
30- 34					4*	1		
25- 29					3		1	2
20- 24					6	4	2	1
15- 19						4*		
10- 14						7	4	1
5- 9						2	9*	4
0- 4							4	14*

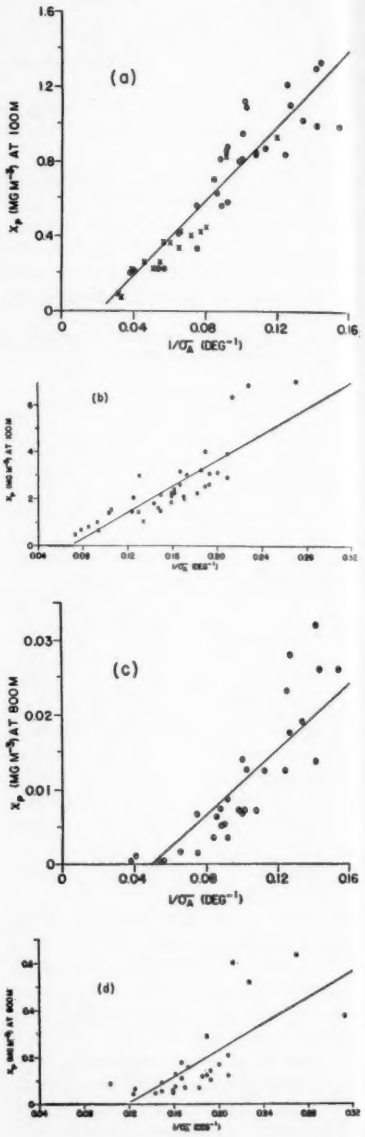


Fig. 6. Peak concentration at 2 travel distances versus inverse standard deviation of azimuth wind direction. Daytime gas releases are shown in (a), (c); nighttime gas releases are presented in (b), (d). Round Hill data are indicated by symbol x in (a), (b).

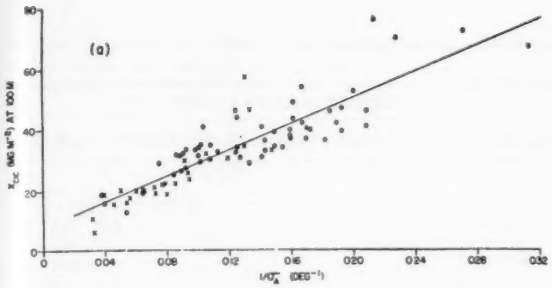
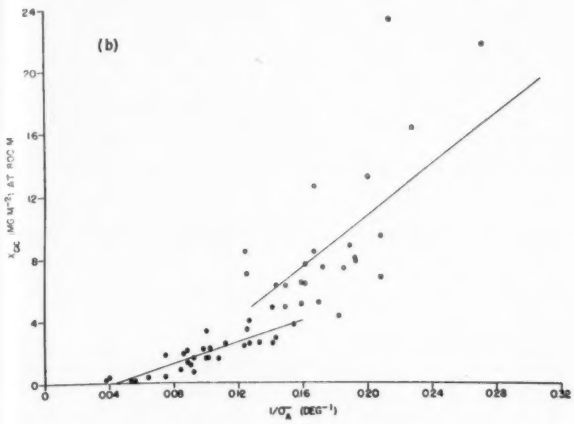


Fig. 7. Integrated-crosswind concentration at 2 travel distances versus inverse standard deviation of azimuth wind direction. Round Hill data are indicated by symbol x in (a); upper regression line in (b) refers to nighttime gas releases (open circles) and lower regression line refers to daytime gas releases (filled circles).



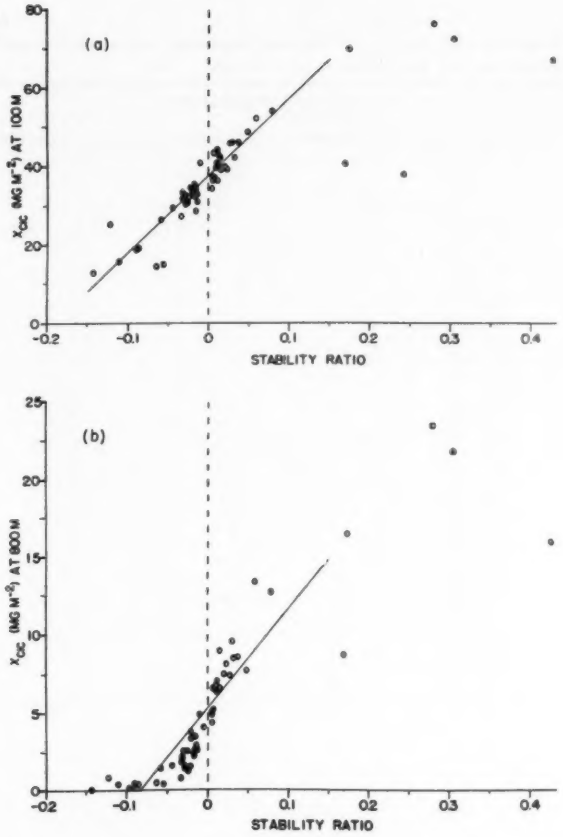


Fig. 8. Integrated-crosswind concentration at 2 travel distances versus stability ratio.

TABLE III

Vertical Concentration Profiles at Travel Distance of 100 m. for Nighttime Gas Releases
Entries show frequency distributions of concentration at various sampling heights expressed as percentage of concentration at height of 0.5 m.; median values are indicated by asterisks.

Height (m.)	1.0	1.5	2.5	4.5	7.5	10.5	13.5	17.5
%								
105-109	2							
100-104	4	1						
95- 99	8*	4	1					
90- 94	7	8*	1					
85- 89	3	5	1					
80- 84		2	4					
75- 79		1	4					
70- 74		1	5*					
65- 69		2	3	1				
60- 64				1				
55- 59			1	2				
50- 54				2				
45- 49				4				
40- 44			2	3*				
35- 39			1	4				
30- 34				2				
25- 29			1	1	1			
20- 24					4			
15- 19				1	4			
10- 14					6*			
5- 9				1	4	8		
0- 4				2	5	16*	24*	24*

site is described by Barad[4]. The relationship between standard peak concentration and $1/\sigma_A$ at 2 travel distances is illustrated in Fig. 6; the correlation between the variates is about 0.90 for the daytime experiments and about 0.80 for the nighttime experiments, over the entire 800 m. travel distance. The striking agreement between the Round Hill and Prairie Grass measurements shown in Fig. 6(a), 6(b) is also found at 200 m.; and, at 50 m., if a reasonable adjustment is made for the 2 m. sampling height used at Round Hill. Integrated-crosswind concentration has been plotted against both meteoro-

c. The correlation between the variates is significantly lower at 50 m. than at the other travel distances in both the Round Hill and Prairie Grass measurements.

d. The correlation between the variates is about the same in both sets of data. The regression line for the Round Hill data has approximately the same slope as that for Prairie Grass; however, the intercept at $SR = 0$ is about 50% lower than in Fig. 8(a).

TABLE IV

Frequency Distributions of Power-law exponent, b over 4 Intervals of Travel Distance for Daytime Gas Releases. Median values are indicated by asterisks.

(a) Peak concentration					(b) Integrated-crosswind concentration				
Distance (m.)	(50-100)	(100-200)	(200-400)	(400-800)	Distance (m.)	(50-100)	(100-200)	(200-400)	(400-800)
b					b				
3.90-3.99				1	2.90-2.99				1
3.80-3.89					2.80-2.89				1
3.70-3.79					2.70-2.79				
3.60-3.69				1	2.60-2.69				2
3.50-3.59				1	2.50-2.59				1
3.40-3.49				1	2.40-2.49				
3.30-3.39				1	2.30-2.39			2	
3.20-3.29					2.20-2.29			1	1
3.10-3.19					2.10-2.19			1	1
3.00-3.09				1	2.00-2.09		1		
2.90-2.99	1			1	1.90-1.99		1		1
2.80-2.89			1		1.80-1.89		2	3	
2.70-2.79			1	2	1.70-1.79			1	2
2.60-2.69		1	4		1.60-1.69	1	1	1	4
2.50-2.59	1	2	3	1'	1.50-1.59	2	1	2	3*
2.40-2.49	2	2	4	3	1.40-1.49	1		3	6
2.30-2.39	1	2	4*	5*	1.30-1.39		3	8*	2
2.20-2.29		1	4	1	1.20-1.29	2	1	1	2
2.10-2.19		1	3	5	1.10-1.19	1	1	6	2
2.00-2.09	5	5	2	2	1.00-1.09	2	12*	2	1
1.90-1.99	2	5*	5	2	0.90-0.99	5	1		
1.80-1.89	5*	5	1	2	0.80-0.89	9*	5		
1.70-1.79	9	4		1	0.70-0.79	6	1		1
1.60-1.69	5	3		1					
1.50-1.59	2	1							

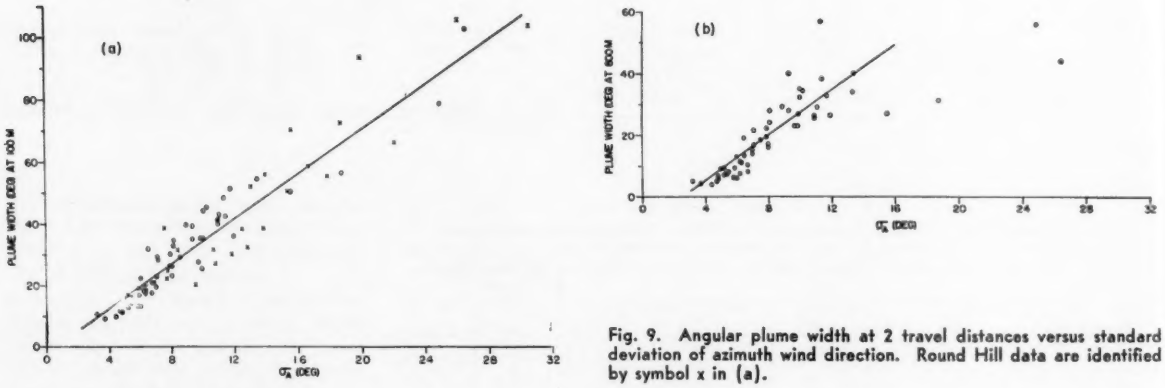


Fig. 9. Angular plume width at 2 travel distances versus standard deviation of azimuth wind direction. Round Hill data are identified by symbol x in (a).

logical parameters in Fig. 7, 8. A high correlation is expected between χ_{C1C} and *SR* since principal variations in χ_{C1C} occur as a result of vertical flux of plume material. The results show that *SR* is superior to $1/\sigma_A$ as a predictor if cases of extreme thermal stability are excluded. However, $1/\sigma_A$ shows a better relationship over the complete range of observation. The close agreement between the Prairie Grass and Round Hill data shown in Fig. 7(a) is also evident at 50 and 200 m.[c] No Round Hill data are entered in Fig. 8(a) because the results do not fit the Prairie Grass observations; it appears that this discrepancy is due to the influence of site factors on the stability ratio[d]. Improved prediction of peak concentration and integrated-crosswind concentration, particularly for the nighttime experiments, can probably be effected by combining $1/\sigma_A$ and *SR* in a single index.

Angular plume width at 2 travel distances is plotted against σ_A in Fig. 9. To conserve space, data from the daytime and nighttime releases have been combined; the standard error for the nighttime cases considered separately is considerably smaller than the value entered in Table VI. The 3 points to the right of the regression line in Fig. 9(b) illustrate the effect of extreme dilution on angular plume width at 800 m. As shown by the data in Fig. 6(b), 7(b) concentrations at 800 m. become almost negligible for $\sigma_A > 16°$. The correlation between the standard deviation of concentration at the 5 travel distances and σ_A has not been computed, although a close relationship is anticipated[e]. Changes with distance in both peak and integrated-crosswind concentration are highly correlated with $1/\sigma_A$. In Fig. 10, the

[e] Approximate values for the standard deviation of concentration are obtained by dividing angular plume width by 4.3.

TABLE V

Frequency Distributions of Power-law Exponent b over 4 Intervals of Travel Distance for Nighttime Gas Releases. Median values are indicated by asterisks.

(a) Peak concentration					(b) Integrated-crosswind concentration				
Distance (m.)	(50-100)	(100-200)	(200-400)	(400-800)	Distance (m.)	(50-100)	(100-200)	(200-400)	(400-800)
b					b				
2.00-2.04			1		1.15-1.19				1
1.95-1.99					1.10-1.14			2	
1.90-1.94					1.05-1.09				2
1.85-1.89				1	1.00-1.04			1	
1.80-1.84			1	2	0.95-0.99			2	1
1.75-1.79		1		1	0.90-0.94		1	3	3
1.70-1.74		2	1	1	0.85-0.89		6	5*	2
1.65-1.69		6	2		0.80-0.84		7*	2*	4*
1.60-1.64	2	2	4	2	0.75-0.79	4	5	3	8
1.55-1.59	1	5*	2	1	0.70-0.74	5	2	5	1
1.50-1.54	5		5*	3	0.65-0.69	7*	2	1	
1.45-1.49	4*	3	3	4*	0.60-0.64	1	2	2	
1.40-1.44		2	4	1	0.55-0.59	4	1		2
1.35-1.39	3	2		1	0.50-0.54	1	1		1
1.30-1.34	2			3	0.45-0.49				
1.25-1.29	4		1		0.40-0.44	1			
1.20-1.24	1	1	1	3					
1.15-1.19	1		2	1					
1.10-1.14		2							
1.05-1.09		1		1					
1.00-1.04				1					

power-law exponent b for the 100-400 m. interval of travel distance is plotted against $1/\sigma_A$; the upper regression line refers to peak concentration and the lower line is for integrated-crosswind concentration. The slight convergence of the regression lines from an initial separation of about unity (as measured on the ordinate scale) reflects differences in the ratio of peak concentration to average plume concentration between the daytime and nighttime gas releases.

Although investigation of empirical relations between diffusion and various meteorological parameters is incomplete, the preliminary results described above show rather conclusively that simple meteorological parameters are useful diffusion predictors over travel distances of about 1 km. from continuous point sources near ground level. For many practical applications, satisfactory diffusion estimates may be obtained from a knowledge of the mean wind speed and the frequency distribution of azimuth wind direction. It appears likely that the addition of the frequency distribution of elevation angle to these meteorological parameters will permit satisfactory estimates of diffusion from elevated sources.

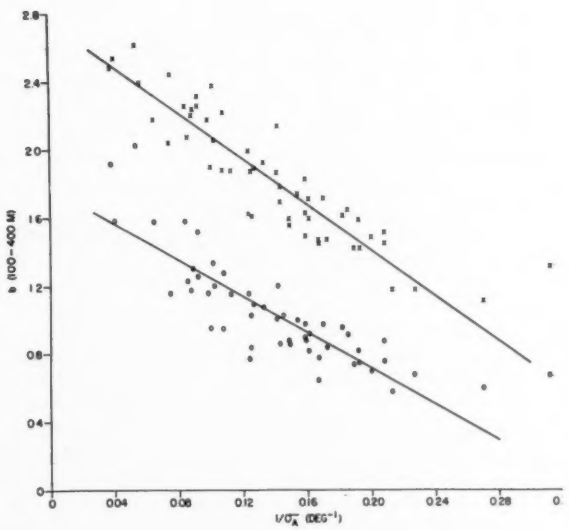


Fig. 10. Power-law exponent b for 100-400 m. distance interval versus inverse standard deviation of azimuth wind direction. Upper regression line refers to peak concentration and lower regression line is for integrated-crosswind concentration.

Acknowledgment

The authors wish to express their appreciation to Dr. M. L. Barad, field director of Project Prairie Grass, and to the many people who assisted in the diffusion measurements. Mr. H. C. Vaughan was responsible for the meteorological instrumentation. Other members of the staff of the Round Hill Field Station who made vital contributions to the experimental program include George Fontes, Harry V. Geary, John E. Luby, and J. H. Peers. Observations of vertical profiles of mean wind speed and air temperature were made available by Prof. Maurice H. Halstead of Texas A & M. The authors wish to thank Prof. H. G. Houghton for his interest and support, and for reading the manuscript.

TABLE VI

Linear Correlation Coefficients r and Standard errors of Estimate Sy for Empirical Relations between Basic Plume Characteristics and 2 Meteorological Parameters; n= sample size.

Variates	*Fig.*	*r*	S_y	*n*
(1) σ_A, χ_P at 100 m. (daytime)	6(a)	0.93	0.13 mg./m.^{3}	(45)
(1) σ_A, χ_P at 100 m. (nighttime)	6(b)	0.86	0.86	(39)
(1) σ_A, χ_P at 800 m. (daytime)	6(c)	0.87	0.0044	(30)
(1) σ_A, χ_P at 800 m. (nighttime)	6(d)	0.73	0.11	(27)
(1) σ_A, χ_{CIC} at 100 m.	7(a)	0.88	6.35 mg./m.^{3}	(81)
(1) σ_A, χ_{CIC} at 800 m. (daytime)	7(b)	0.86	0.63	(30)
(1) σ_A, χ_{CIC} at 800 m. (nighttime)	7(b)	0.69	3.60	(25)
SR, χ_{CIC} at 100 m.	8(a)	0.92	3.65	(50)
SR, χ_{CIC} at 800 m.	8(b)	0.87	1.64	(51)
σ_A, W at 100 m.	9(a)	0.95	7.1°	(82)
σ_A, W at 800 m.	9(b)	0.85	6.2	(53)
(1) σ_A, b_P (100-400 m.)	10	−0.92	0.14	(53)
(1) σ_A, b_{CIC} (100-400 m.)	10	−0.85	0.16	(51)

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Specifications Required for Design of Electrostatic or Combination Mechanical - Electrostatic Collectors for Fly Ash Collection from Boiler Gases

ELECTROSTATIC PRECIPITATION SUB-COMMITTEE

S. W. Randolph, Chairman

The diverse and unpredictable properties of fly ash, as well as the increasing demands on gas cleaning equipment, have complicated design considerations for both electrostatic and mechanical collectors in spite of advances and improvements in collector technology. Closer cooperation between users and designers of such equipment is necessary to achieve mutually satisfactory solutions to problems in this field. As a result of this situation, it is imperative that prospective purchasers of fly ash collection equipment supply prospective bidders with essential information for design purposes.

The following specification or request for bids covers the essential data required by the manufacturers of fly ash collectors to intelligently analyze each problem. Any additional data which the purchaser can supply will be helpful to bidders. Also, a list of questions, the answers to which the purchaser would like to have to properly analyze the bids, should be attached to the request for bids.

A specification or request for bids should:

(*1*) State the efficiency to be guaranteed.

(*2*) State whether bids are requested for:

a. Combination mechanical and electrostatic collector.

b. Electrostatic collector only.

c. Both (a) and (b).

d. If no preference, so state.

The following report is the result of comprehensive study by the Electrostatic Precipitation Sub Committee of Committee T-12. The chairman of the Sub Committee was S. W. Randolph and the chairman of T-12 (now designated as TA-5) was J. T. Doyle.

The report was first submitted to the Technical Council, and after revision, was again sent to the Council which approved it in its present form. The Board of Directors, on May 25, 1958, authorized publication.

(*3*) State maximum permissible pressure drop in inches of water at guarantee point and give evaluation rate in dollars per inch of pressure drop.

(*4*) Specify barometric pressure at plant site or elevation above sea level.

(*5*) Specify the steam output of the boiler and the volume, temperature, pressure and moisture content of the gas, at the inlet of the collector, at the minimum boiler rating, maximum continuous rating and peak rating and state at which rating the guarantee is to apply ("Guarantee point").

(*6*) Specify gas analysis at guarantee point.

(*7*) Specify the total concentration of suspended matter in gas in grains/ft.^{3} at standard conditions (32° F. and 29.92" Hg.) at the guarantee point and at any other points at which performance data is requested.

(*8*) Particle size consist and resistivity of the dust, using methods outlined in Appendix III and II, respectively.

(*9*) Specify specific gravity of the dust, both bulk and particle.

(*10*) Specify nature or chemical analysis of the dust, using method outlined in Appendix No. I —

a. Water soluble content of dust.

b. Water soluble sulphate content of dust

c. Combustible content of of dust

(*11*) State electric power characteristics; i.e., AC, DC, voltage, phase, frequency and voltage regulation.

(*12*) Indicate space available and supply drawings showing building and equipment layout, including location of air heaters, dust collecting equipment, fans and stack.

(*13*) For coal-fired boilers give following information on coal:

a. Source or sources of coal and whether deep-mined or strip-mined.

b. State whether sources are changed frequently.

c. Coal analysis (as fired),

including ash, fixed carbon, moisture, sulphur and volatile matter. This should be supplied for each of the coals to be used, together with a statement of which type coal will be generally fired and on which the efficiency guarantee is to apply.

d. Size consist of the pulverized coal and type of pulverizer.

e. Lbs./hr. of coal burned at minimum boiler rating, maximum continuous rating, and at peak rating.

f. Are any other fuels to be fired? State what kind, how much, and under what conditions.

(*14*) Give following information regarding boiler:

a. Boiler manufacturer and type of furnace

b. Dry or wet bottom

c. Number and type of burners

d. Number and type of air preheaters

e. Expected duty cycle of boiler (base load or swing load)

f. Will there be a by-pass around the superheater?

g. State type of ash disposal system and operating cycle.

Appendices

It is recognized that there has not been, until recently, general agreement on methods of chemical analysis of fly ash, nor on methods of determining resistivity and particle size. The attached appendices are the results of careful study to establish such standard methods.

Appendix I outlines the approved method of chemical analysis covering —

a. Water soluble content

b. Water soluble sulphate content

c. Combustible content

Appendix II covers the approved method of determining the resistivity ticle size distribution of fly ash.

Appendix III will cover the approved method of determining particle size distribution of fly ash. Studies are now under way on this subject and the results will be incorporated as this appendix as soon as they are available.

It is also realized that the prospective purchaser may not always have equipment available to make the chemical analyses and the resistivity and particle size determinations. In such cases, it is suggested that the purchaser furnish identical samples of the fly ash to each of the bidders and to request each to submit the results of the analyses and the determinations.

Appendix I

Approved Standard Methods for the Determination of Loss on Ignition, Water Soluble Content and Water Soluble Sulfate Content of Fly Ash

Sample Preparation:

(*1*) A representative sample of approximately 10 g. of the fly ash shall be dried in an oven at a temperature of 105 to 120° C. for one hour.

(*2*) Cool and store the dried sample in a desiccator.

(*3*) Conduct all analyses in duplicate.

Loss On Ignition:

(*4*) Transfer 1 g. of dried sample to a pre-ignited and weighed 10 to 30 ml. capacity porcelain crucible. A crucible having a large surface area on the bottom is preferred.

(*5*) Ignite the crucible and its contents with free access of air to constant weight in a muffle furnace at a temperature of 800° ±50° C.

(*6*) Calculation—Calculate the percentage of loss on ignition to the nearest 0.1% by multiplying the loss of weight in grams by 100.

Water Soluble Content:

(*7*) Weigh a 1 g. sample of the dried fly ash. Using a wash bottle with a fine stream of water, carefully wet and transfer the sample to a 200 ml. or 300 ml. beaker. Increase the volume of water to approximately 125 ml.

(*8*) Boil gently for 15 min. Remove from the heat, wash cover glass and walls of beaker down with hot water.

(*9*) Using vacuum, filter through a pre-dried weighed porcelain Gooch crucible containing an asbestos mat. (Alternately a glass Gooch crucible containing a fritted glass bottom of fine porosity may be used.) Catch the filtrate in a clean, properly trapped vacuum flask. Carefully police all particles from the beaker and wash the beaker and crucible well with hot water. Save filtrate for the sulfate determination.

(*10*) Dry the crucible in an oven at 105 to 120°C. for 1 hr. Cool in a desiccator and weigh rapidly.

(*11*) Calculations—% water soluble =(Wt. sample—Wt. of insoluble) × 100.

Water Soluble Sulfate:

(*12*) Transfer the filtrate from step 9 to a tall 400 ml. beaker (or other suitable container). Add 3 ml. of concentrated HCl. Increase the volume to 300 ml. and bring to a boil.

(*13*) Remove from the heat and while stirring vigorously, slowly add 10 ml. of $BaCl_2$ solution 100 g./*l.*) Allow beaker to set for at least two hr., with periodic stirring at a temperature between 50 to 70°C.

(*14*) Filter through a fine grade of filter paper or through a pre-ignited weighed Gooch crucible. Police beaker well as the $BaSO_4$ tends to adhere to the walls and bottom of the beaker. Wash well with hot water.

(*15*) Dry and ignite the Gooch over a Bunsen burner or in a muffle for ½ hr. If a filter paper is used, the paper should be charred carefully and ignited with free access of air. Cool in a desiccator and weigh as $BaSO_4$.

(*16*) ***Calculation:***
% Water Soluble Sulfate:
(Identify result as either % SO_3 or % SO_4)
as SO_4 = Wt. $BaSO_4$ × 41.15
as SO_3 = Wt. $BaSO_4$ × 34.30

Approved Alternate Method For Determination of Water Soluble Sulfate Content of Fly Ash

The following alternate method for determination of Water Soluble Sulfate Content of Fly Ash is preferred

by some analysts because of its time saving features.

Procedure

Transfer the filtrate from Step 9 under Water Soluble Content to a 250 ml. volumetric flask and make up to volume with distilled water.

Determination of Calcium and Magnesium

Reagents

(*1*) Versenate solution (0.01 M.). Dissolve 3.72 g. of the disodium salt of ethylenedinitrilo tetracetic acid dihydrate in distilled water and dilute to 1 *l.* Standardize this solution against a standard calcium solution.

(*2*) Standard calcium solution (0.01 M.). Dissolve exactly 1000 g. of pure dried calcium carbonate in 5 ml. of 6 N hydrochloric acid and dilute to 1 *l.* with water.

(*3*) Buffer solution (pH 10). Dissolve 67.5 g. of ammonium chloride in 200 ml. of water, add 570 ml. of concentrated ammonium hydroxide (sp. gr. 0.90), and dilute to 1 *l.* with water.

(*4*) Potassium cyanide, 10% (W/V). Dissolve 10 g. of potassium cyanide in 100 ml. of water.

(*5*) F 241 indicator. Dissolve 0.15 g. of Eriochrome Black T and 0.5 g. of sodium borate in 25 ml. of methanol.

(*6*) Standard magnesium chloride solution (0.01 M.). Dissolve 2.03 g. magnesium chloride hexahydrate in distilled water and dilute to 1 *l.* Determine the ratio of 0.01 m. $MgCl_2$ solution to 0.01 M versenate solution.

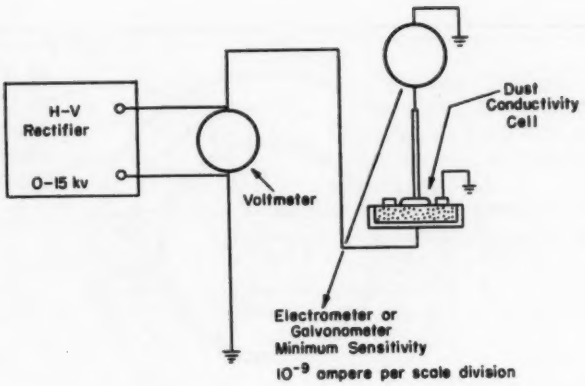

FIG. 2

Titration Procedure

Pipette 50 ml. aliquot from the 250 ml. volumetric flask into a 250 ml. Erlenmeyer flask. Add 5 ml. of buffer solution, 1 ml. of 10% KCN solution and 8 drops of F 241 indicator. Add exactly 3 ml. of 0.01 M $MgCl_2$ solution and titrate rapidly with 0.01 M versenate solution to endpoint. The endpoint is reached when the color changes from wine red to blue. Add exactly 2 ml. of 0.01 M $MgCl_2$ solution and titrate carefully with 0.01 M versenate to the endpoint.

Determination of Sulfate

(*1*) Standard $BaCl_2$ solution (0.01 M.). Dissolve 2.44 g. of barium chloride dihydrate in distilled water and make to 1 *l.* Determine the ratio of 0.01 M $BaCl_2$ solution to 0.01 M versenate solution.

(*2*) All other reagents are the same as in determination of calcium and magnesium.

Titration Procedure

Pipette 50 ml. aliquot from the 250 ml. volumetric flask into a 250 ml. Erlenmeyer flask. Add 6 N HCl until slightly acid. Boil the sample and add an accurately measured quantity of 0.01 M $BaCl_2$ solution (about 10-20 ml. depending on estimate of sulfate) and allow the mixture to boil for 2-3 min. Cool and add 4-5 ml. of buffer solution, 1 ml. of 10% KCN, and 8 drops of F 241 indicator solution. Add exactly 3 ml. of 0.01 M $MgCl_2$ solution and titrate rapidly with 0.01 M versenate to the endpoint. Add exactly 2 ml. of 0.01 M $MgCl_2$ solution and titrate carefully with 0.01 M versenate to the blue endpoint.

Calculations

A=molarity of versenate solution.
B=milliliters versenate equivalent to total ml. of $MgCl_2$ solution used (5 ml.).
C=milliliters versenate equivalent to ml. of $BaCl_2$ solution used.
D=milliliters versenate equivalent to calcium and magnesium in aliquot.
E=total milliliters versenate used in sulfate titration.
F=sample weight used.

% Water Soluble Sulfate:

as

$$SO_4 = \frac{(B+C+D-E)\times A\times 1.20}{F}$$

Note

When reporting Water Soluble Sulfate Content of Fly Ash, state which of the above approved methods for determination was employed.

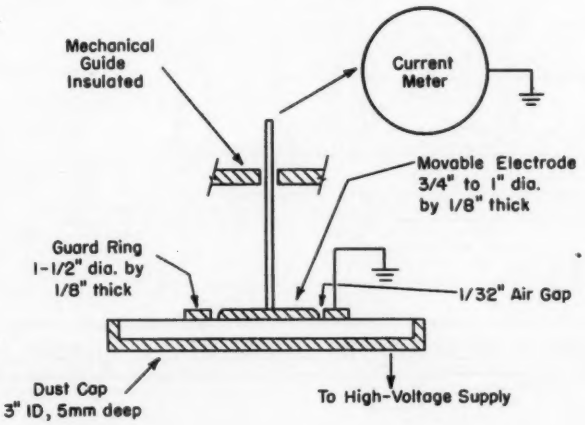
Mechanical Guide Insulated
Current Meter
Movable Electrode 3/4" to 1" dia. by 1/8" thick
Guard Ring 1-1/2" dia. by 1/8" thick
1/32" Air Gap
Dust Cap 3" ID, 5mm deep
To High-Voltage Supply

FIG. 1

Appendix II

Approved Standard Method For Determination of Bulk Electrical Resistivity of Fly Ash

The electrical resistivity of fly ash shall be determined by means of a high-voltage conductivity cell having the basic dimensions shown in Fig. 1. Two accepted methods of construction are shown in Fig. 3 and 4.

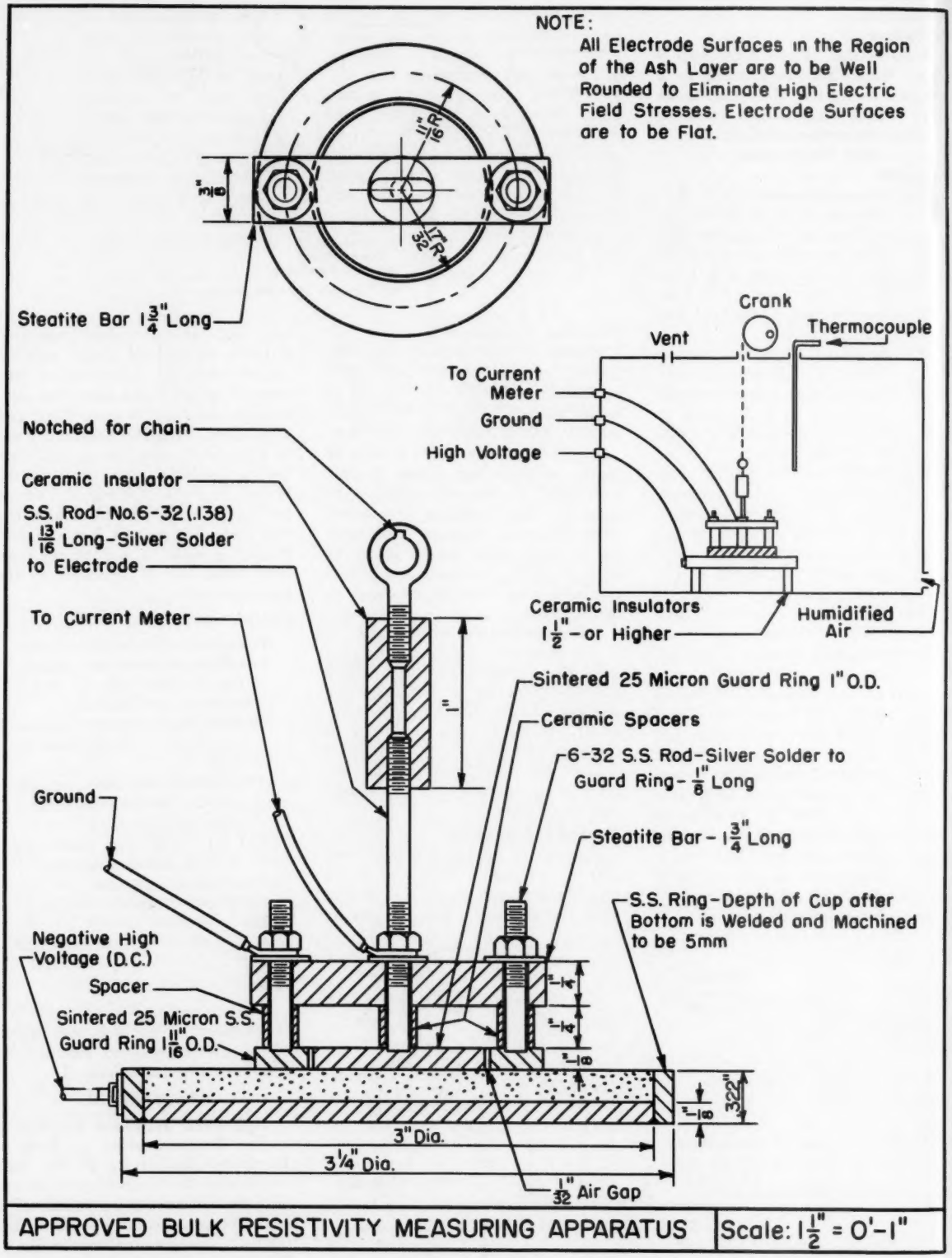
NOTE:
All Electrode Surfaces in the Region of the Ash Layer are to be Well Rounded to Eliminate High Electric Field Stresses. Electrode Surfaces are to be Flat.
11/16" R
17/32" R
Steatite Bar 1 3/4" Long
Crank
Vent
Thermocouple
To Current Meter
Ground
High Voltage
Notched for Chain
Ceramic Insulator
S.S. Rod-No.6-32 (.138) 1 13/16" Long-Silver Solder to Electrode
To Current Meter
Ceramic Insulators 1 1/2" - or Higher
Humidified Air
Sintered 25 Micron Guard Ring 1" O.D.
Ceramic Spacers
6-32 S.S. Rod-Silver Solder to Guard Ring - 1/8" Long
Steatite Bar - 1 3/4" Long
S.S. Ring-Depth of Cup after Bottom is Welded and Machined to be 5mm
Ground
Negative High Voltage (D.C.)
Spacer
Sintered 25 Micron S.S. Guard Ring 1 11/16" O.D.
3/32"
3/32"
3/32"
3/32"
3" Dia.
3 1/4" Dia.
1/32" Air Gap
APPROVED BULK RESISTIVITY MEASURING APPARATUS
Scale: 1 1/2" = 0'-1"

FIG. 3

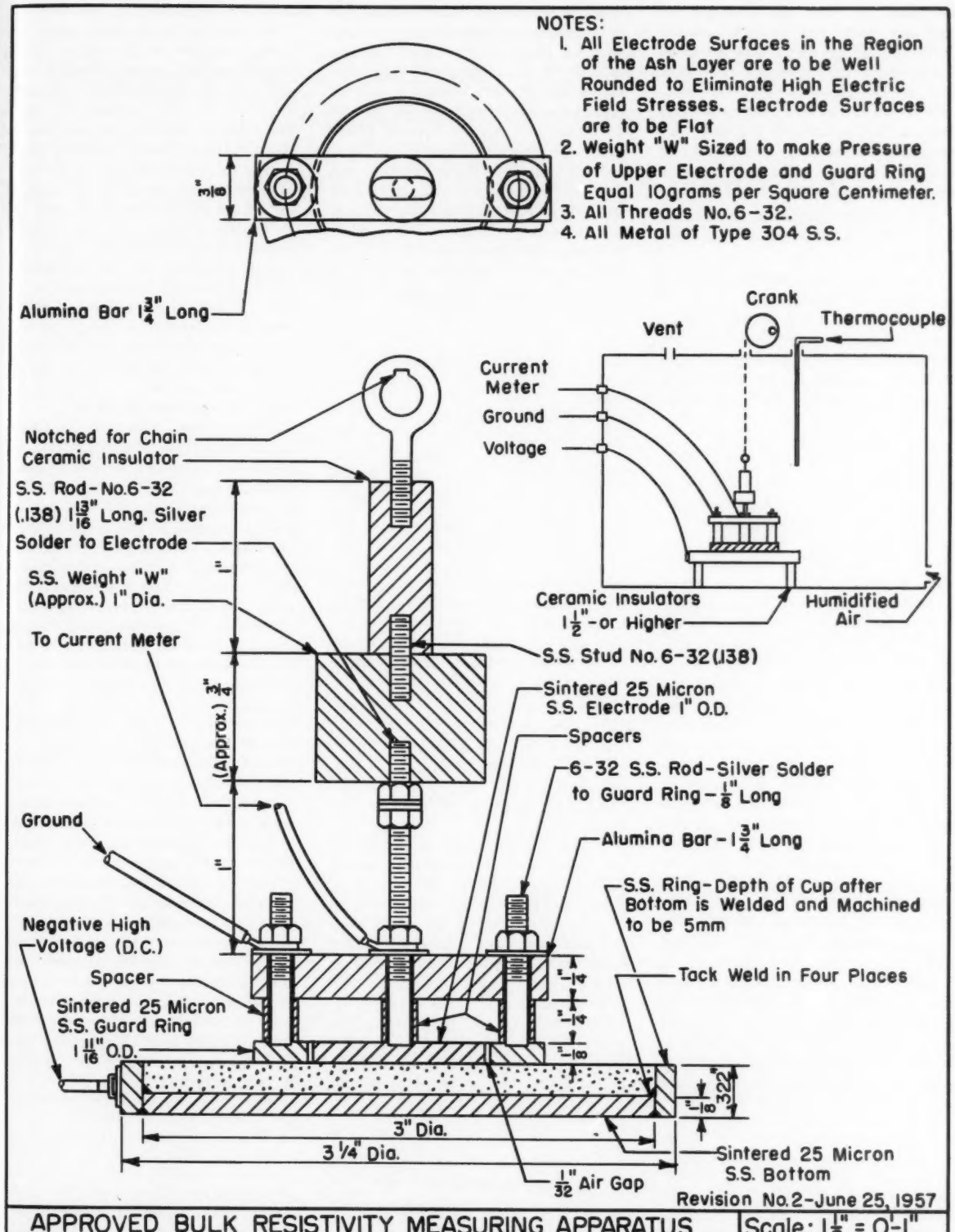
NOTES:
1. All Electrode Surfaces in the Region of the Ash Layer are to be Well Rounded to Eliminate High Electric Field Stresses. Electrode Surfaces are to be Flat
2. Weight "W" Sized to make Pressure of Upper Electrode and Guard Ring Equal 10grams per Square Centimeter.
3. All Threads No.6-32.
4. All Metal of Type 304 S.S.
Alumina Bar 1 3/4" Long
Crank
Vent
Thermocouple
Current Meter
Ground
Voltage
Notched for Chain
Ceramic Insulator
S.S. Rod-No.6-32 (.138) 1 13/16" Long. Silver Solder to Electrode
S.S. Weight "W" (Approx.) 1" Dia.
To Current Meter
1"
3/4" (Approx.)
1"
Ceramic Insulators 1 1/2"-or Higher
Humidified Air
S.S. Stud No.6-32(.138)
Sintered 25 Micron S.S. Electrode 1" O.D.
Spacers
6-32 S.S. Rod-Silver Solder to Guard Ring-1/8" Long
Alumina Bar-1 3/4" Long
Ground
S.S. Ring-Depth of Cup after Bottom is Welded and Machined to be 5mm
Negative High Voltage (D.C.)
Tack Weld in Four Places
Spacer
Sintered 25 Micron S.S. Guard Ring 1 11/16" O.D.
1/4"
1/4"
1/8"
1/8"
.322"
3" Dia.
3 1/4" Dia.
Sintered 25 Micron S.S. Bottom
1/32" Air Gap
Revision No.2-June 25, 1957
APPROVED BULK RESISTIVITY MEASURING APPARATUS
Scale: 1 1/2" = 0'-1"

FIG. 4

The movable disc electrode is weighted so that the pressure on the ash layer due to gravitational force is 10 g./cm^2. The nominal thickness of the ash layer is 5 mm. The actual thickness is to be determined with movable electrode resting on the surface of the ash. All electrode surfaces in the region of the ash layer are to be well rounded to eliminate high electric field stresses.

The electric circuit for determination of the resistivity is shown schematically in Fig. 2.

The high-voltage rectifier is rated for 0 to 15 kv. voltage output at currents up to one milliamp. with a total ripple not exceeding 1%. The current meter may be either an electrometer or a galvanometer having a sensitivity of at least 10^{-9} amp./scale division.

The measurement method is as follows: fly ash is placed in the cup of the conductivity cell by means of a spatula and levelled by drawing a straight edge blade vertically across the top of the cup. It will be noted that this method of filling may introduce slight variations in the initial packing of the ash in the cup. However, tests indicate that this effect is relatively small for the large majority of ashes encountered in practice.

The disc electrode is then gently lowered onto the surface of the ash. Under these conditions the disc electrode should rest freely on the ash surface and without binding in its support. The guard ring may be attached physically to the movable disc electrode by means of suitable high temperature insulators, e.g. mica, silica, or alumina, or it may be mounted and guided separately. In general, the latter arrangement is to be preferred since there will be a free air gap between the guard ring and the movable disc electrode with no possibility of current leakage between the two. The annular spacing of approximately 1/32-in. between the guard ring and movable disc electrode is ample provided the mechanical supports or guide means are accurately made. The details of accomplishing this are not shown inasmuch as this is a matter of convenience in mechanical design rather than a fundamental factor. Resistivity measurements for fly ash normally will be made at a temperature of 300°F. and a humidity of 5% by volume unless otherwise specified. Since the voltage-current characteristics of the ash cell are non-linear, the resistivity shall be calculated using corresponding values of voltage and current at a voltage in the range of 85% to 95% of the breakdown value. The value of the resistivity shall be calculated using the formula

$$r = \frac{V}{I} \cdot \frac{A}{L}$$

where

r=resistivity (ohm. cm.)

L=actual thickness of ash layer between electrode surfaces (cm.)

A=cross-sectional area of electrode connected to electrometer (cm.^{2})

$$= \frac{\pi d^2 (cm.^2)}{4}$$

d=diameter of disc electrode in contact with dust as shown in Fig. 1 (cm.)

V=applied voltage (volts)

I=current corresponding to voltage V (amp.)

For measurements at elevated temperatures and controlled humidity, the resistivity cell is mounted in an electric oven with thermostatic temperature control and well heat insulated to maintain uniform internal temperature.

Humidity may be controlled by any one of several conventional means including circulation of pre-conditioned gas through the oven, injection of controlled amount of steam, temperature-controlled circulated water bath, or by certain chemical solutions which control vapor pressure. To provide intimate contact between the humidified gas and the dust in the resistivity cell, it is desirable to circulate the humidified gas directly through the dust layer. This should be done by using sintered stainless-steel electrodes of 25 μ porosity.

In making a measurement, the voltage applied to the cell is raised from zero in a series of small steps and the current through the ash layer observed for each voltage step up to the point of electrical breakdown of the ash layer. Before making actual resistivity measurement, it is desirable to pre-determine the breakdown voltage of the ash sample. This should be checked by two or three observational runs in which the voltage is raised gradually to the breakdown point. After each breakdown, the ash layer should be remixed and relevelled in order to break up any spark channels which may have been formed through the ash layer. An entirely new sample is preferred for each measurement if possible.

In any case, resistivity measurements at elevated temperatures and controlled humidity should be made under equilibrium temperature and moisture conditions between the gas and the dust. The condition for equilibrium of temperature and moisture conditions in the ash shall be determined by the requirement that resistivity measurements be reproducible within 10% when determined by two successive measurements 15 min. apart. Further, since the particle conductivity usually depends on the past treatment of the particles, as well as on the temperature and humidity equilibrium reached under given conditions, it is preferable to determine the conductivity by raising the oven temperature to the value desired rather than by first heating above the desired temperature and then cooling to the desired temperature.

Strict adherence to the above procedures should insure comparable results by all investigators regardless of minor variations in the apparatus employed. It is believed, however, that standardization of apparatus as well as procedure should further contribute to uniformity of results. The following details of an approved form of apparatus are therefore included in this Appendix.

Atmospheric Pollution: The Role Played by Combustion Processes

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Introduction

Human awareness of the problem of air pollution dates back at least as early as 75 A.D., when Pliny referred to the harmful effects of dust exposure. (1) Up until the past century or so, before the rapid growth of the chemical and related industries, chief concern regarding air pollution was doubtless given to the nuisance aspects of smokes from combustion processes. For example, as early as 1273 Parliament passed an act prohibiting the burning of coal in London, and in 1306 an artificer was tried, condemned, and executed for this offense. (2) Evidently this law was later relaxed. The emission of smoke has long since become recognized as a sign of inefficient, uneconomical combustion and, therefore, is generally avoided in large industrial operations. Unfortunately, this is all too frequently untrue in the case of small-scale industrial operations and domestic heating installations.

The first dramatic cases of air pollution probably arose during the period of early growth of the chemical and related industries. During this period, noxious waste gases were carelessly discharged into the atmosphere, with the resulting devastation of the surrounding vegetation and physical discomfort (to say the least) of the surrounding inhabitants. One hestitates even to speculate upon the severity of the health hazards to which workmen directly associated with operations were exposed during this period of technological immaturity, especially with regard to industrial hygiene and safety.

Public and legal pressure probably instigated the first remedial steps taken by industry to overcome these acute problems of air pollution by preventing, in one way or another, the emission of noxious materials into the atmosphere. It was probably soon learned that the value of the pollutants recovered or otherwise prevented from escaping to the atmosphere, usually far exceeded the cost of the measures required to prevent air pollution, even without regard to humanitarian or aesthetic considerations. From this time on, chemical and related industries have found it expedient to provide against air pollution in the design of any new operation before its erection. It is encouraging to note that increasing consideration is being given by industry in general to the humanitarian and aesthetic aspects of air pollution in addition to its direct economic aspects.

In the combustion industries, there has been an understandable, but not excusable, lag in the prevention of air pollution because of insufficient economic incentives. The prevention of smoke has long been recognized to be an economically wise policy, but the removal of other pollutants from combustion processes, especially sulfur dioxide, has not yet given sufficient promise of being justifiable from purely direct economic considerations. Yet combustion processes are the major over-all source of air pollution.

Air Pollution Disasters

During the past quarter of a century, four major disasters resulting from air pollution have been recorded, each of which was associated with severe physical disorders, including numerous fatalities.

Meuse Valley Disaster (3, 4)

In December 1930, during a heavy fog of five days' duration in the valley of the Meuse River in Belgium, between Liege and Huy, seventy persons died and several hundred suffered severe respiratory disorders. The symptoms of distress became evident, generally, on the third day of the smog, as it approached maximum density, and disappeared when the fog lifted. Unusual meterological conditions resulted in a temperature inversion which created an atmospheric ceiling of only around 300 ft., lower than the hills bordering this valley. The air was almost motionless, except for a feeble wind from the direction of the Liege industrial area which caused a slow drift of fumes into this narrow bottleneck valley, only about one-half mile wide.

An investigating commission concluded that sulfur compounds emitted into the air (mainly from the combustion of coal averaging 1% sulfur), caused this disaster. By calculation, the committee estimated that the concentration of sulfur dioxide in the atmosphere could have reached a maximum of about 9 ppm. after the first day of fog and about 35 ppm. after four days.

Donora-Webster Disaster (3, 5, 6)

Late in October 1948, a similar smog disaster occured at two small adjacent communities, Donora and Webster, Pennsylvania. For about five days, beginning October 27, an unusual temperature inversion and still air caused a steady buildup of atmospheric contaminants from zinc smelting, steel, and wire industries,

railroads, river steamboats, and homes. By October 30, illnesses and fatalities began to mount rapidly. The final toll was at least 20 deaths and 5910 cases of sickness, about 43% of the population being involved. The predominant symptom was irritation of the respiratory tract, which was especially severe in elderly persons. The dead ranged in ages from 52 to 85 yr., with a mean age of 65.

A thorough investigation by the United States Public Health Service, conducted in cooperation with local and state authorities and consultants of industrial companies, concluded that this disaster could have been produced by a combination of several contaminants, chief among which was sulfur dioxide and its oxidation products. For example, near a zinc smelting plant was a 5-mile area where tree growth had been devastated by past excessive ground concentrations of sulfur dioxide. Other possible contaminants which were studied were oxides of nitrogen, fluorides, chlorides, hydrogen sulfide, cadmium oxide, and other particulate effluents.

The Donora incident is probably greatly responsible for the vastly increased intensity with which the problem of air pollution has been investigated during the past decade or so.

Poza Rica Disaster [3, 7]

On November 24, 1950, in Poza Rica, Mexico, a city of 22000 persons, mechanical or human misoperation of a natural gas purification plant permitted hydrogen-sulfide-rich gases to escape to the atmosphere for 20 min. during a period of temperature inversion. Twenty-two persons died and 320 people were hospitalized as a result of acute exposure to the hydrogen-sulfide laden atmosphere.

London Disaster of December 1952 [8, 9][a]

During the period December 5-9, 1952, fog or smog covered upward of 1000 sq. mi. of the Thames Valley including London. Visibility was exceptionally low over most of the area, the smog was particularly dirty, and many people experienced difficulty in breathing, and many died of respiratory troubles. The smog in London lasted between 4 and 5 days,

[a] According to Ref. 8 and 10, there was also a 5- to 6-day smog in London in November 1948, which caused about 300 deaths, but in so large a community this incident passed almost unnoticed.

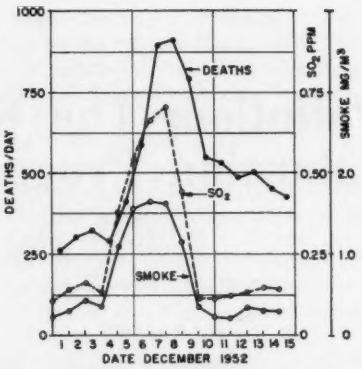

Fig. 1 Daily air pollution and deaths during greater London smog of December 1952. [8]

but the affected people recovered slowly, many not at all.

Fig. 1 shows a striking correlation between rate of fatalities and severity of atmospheric pollution as measured by the average daily concentrations of sulfur dioxide and smoke determined for the entire area preceding, during, and following the smog of December 1952. At the peak of the smog, daily average concentrations of 1.6 mg. m. [3] of smoke and 0.7 ppm. of sulfur dioxide (or five and six times normal concentrations for the area) were reached. Maximum daily average concentrations of 4.5 mg./cu.m. [3] of smoke and 1.34 ppm. of sulfur dioxide were observed at County Hall, Lambeth. By the end of the two-week period following the December 1952 smog, about 4000 people had died in Greater London for reasons attributed to the smog. Further evidence indicates that the period of abnormally high death rates shown in Fig. 1 was followed by another of less intensity but which lasted through most of January and February 1953. The number of extra deaths reported for this period (which was paralleled by generally rising level of pollution, which eventually reached about twice the normal level for that time of year) was of the order of 8000, or about twice that observed during the December peak. It is thus speculated that these latter deaths may have resulted from a second pollution shock to Londoners whose powers of resistance may have been reduced by the December smog. The counter-suggestion has also been made that these additional deaths may have been caused by factors other than of air pollution (*e.g.*, an outbreak of influenza).

In each of the incidents reported above (except for the Poza Rica incident, which was directly attributed to an operational failure within a specific industrial plant), the common meteorological and topographical factors were a steady buildup of pollutants during a period of about five days, a prolonged temperature inversion accompanied by little air movement, and location of the polluted area in a valley surrounded by low hills which retarded horizontal displacement of the polluted atmosphere. In proportion to the populations of the affected areas, the death rates reported for the Meuse Valley, Donora-Webster, and the 1952 London disasters are comparable. [8]

Nature and Causes of Air Pollution

Air pollution has been defined [5] as the excessive concentration of foreign matter or contaminants in the air which adversely affects the well-being of the individual or causes damage to property. The contaminants of air may be classified into two types: (1) materials that exist as gases or vapors, and (2) those that form aerosols. Gases or vapors include the permanent gases as well as compounds that boil below about 300°C., which, when present in low concentrations, exist only as vapor. Aerosols are suspensions of finely-divided solid or liquid particles in air for which the rate of fall is small compared to the Brownian movement or turbulent diffusion.

In approximate order of prevalence and importance in air pollution, the common gaseous contaminants include sulfur dioxide and its oxidation products, (sulfur trioxide and sulfuric acid), hydrogen sulfide, oxides of nitrogen, ammonia, hydrogen fluoride, hydrogen chloride, organic chlorides, carbon dioxide, carbon monoxide, other components in exhaust gases from combustion processes, organic peroxides, and ozone. These contaminants result from combustion of fuels, smelting operations, refineries, chemical plants, pulp mills, sewage disposal plants, incinerators, mine seepages, stockyards, and numerous other sources, including the photochemical oxidation in sunlight of hydrocarbons and other organic vapors which escape into the atmosphere from a variety of sources. Gaseous contaminants cause or contribute to a variety of physiological effects, including eye, nose, throat, and lung irritations, dizziness, paralysis, nausea, and edema, plant and

crop damage, corrosion of structural materials, discoloration of paint, etc.

Aersols can be classified as fog, mist, or cloud, smoke, haze, fume, or dust. *Fog, mist,* or *cloud* are made up of particles consisting mostly of water. *Smoke* consists of suspended solid or liquid particles resulting from combustion or destructive distillation processes. *Fumes* generally refer to aerosols of solid or liquid particles resulting from chemical and metallurgical operations. Fumes are commonly generated by the condensation of matter that has been volatilized from the molten state. *Dust* is solid particles released to the atmosphere by natural forces as well as generated by mechanical processes such as crushing, grinding, milling, drilling, demolition, bagging, sweeping, and shoveling. *Haze* generally refers to aerosols of tiny dust particles, although when applied to a Los Angeles smog, haze consists of liquid aerosols as well.

Aerosols are produced by all combustion processes, and hence most industrial plants, power plants, heating plants, incinerators, automobiles, foundries, blast furnaces, among a host of others, contribute aerosols to the atmosphere. Natural aerosols include fogs, spores, pollens, sea sprays, volcanic dusts, and dust dispersed from arid areas. Probably the outstanding physical characteristic of aerosols is that of light scattering with a consequent decrease of visibility.

Aerosols can exert a variety of chemical or bacteriological effects. In addition, aerosols of solid particulates which penetrate the respiratory passages (*e.g.*, finely divided silica and asbestos) often result in pulmonary conditions. [b] With other atmospheric contaminants, aerosols may cause or contribute to physical irritations as a result of synergistic effects (that is, the aerosols may increase the physiological effects of other agents).

The particle size of air contaminants ranges from molecular dimensions for sulfur dioxide and other gases to over 1000 μ (1 mm.) for rain drops. Fig. 2 shows particle size ranges for industrial as well as natural aerosols. Fig. 2 also indicates the ranges of effective operation of present-day types of equipment generally employed for removing particulate matter from gases.

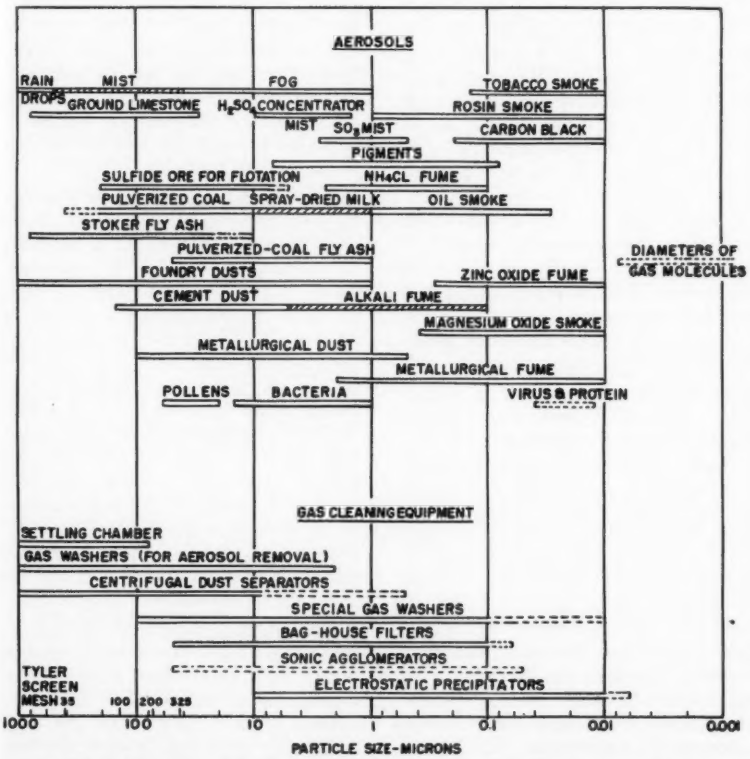

Fig. 2. Particle size ranges of industrial and natural aerosols; effective ranges of operation of equipment for removal of aerosols from gases. (5)

In recent years the term *smog* has become a popular byword. Originally intended to denote a combination of *smoke and fog*, the term smog most frequently refers to the unique atmospheric condition, rarely associated with smoke or fog in the usual sense, which plagues the Los Angeles area some twenty times a year.

In the broadest sense, as applied today, smog refers to an atmospheric condition resulting from the unusual combination of meterological and topographical factors which gives rise to a temperature inversion. Normally, the temperature of the atmosphere decreases as the altitude increases, but under conditions of a temperature inversion, the reverse relationship holds. The stratum of air contained within the elevation range associated with a temperature inversion is referred to as a *temperature inversion layer*. Within a temperature inversion layer, little or no vertical circulation takes place. As a result, in conjunction with topographical conditions such as retard adequate horizontal circulation of the atmosphere (*e.g.*, basin and valley areas), a temperature inversion layer acts as an almost impenetrable canopy which permits the buildup of the air contaminants liberated at ground level to abnormally high and frequently dangerous concentrations.

Weather conditions associated with the Meuse Valley, Donora, and London incidents and with the St. Louis and Pittsburgh areas before enforcement of smoke ordinaces are more nearly representative of the term smog as originally intended. Smoke and fog were definitely present, along with noxious gases such as sulfur dioxide and other aerosols such as fly ash and industrial fumes.

The outstanding characteristics of Los Angeles smog are (1) haze (not fog), which results in a marked reduction in visibility, and (2) the presence of substances that can cause pronounced eye irritation. The haze is caused by finely-divided aerosols in the air, arising from the emission of dust, smoke, and fumes from many industries, the open-air burning of rubbish, the improper functioning of incinerators, incomplete combustion of fuel oils in boiler plants and heating systems, the operation of diesel and automotive engines, etc. Eye irritation is attributed mainly to oxidation products of hydrocarbons. Hydrocarbons enter the atmosphere

[b] See also page 259.

from many sources, such as auto exhausts and losses in the storage, refining, and handling of petroleum products. The photo-oxidation products of hydrocarbons in the atmosphere may produce aerosols that contribute to haze and also aggravate eye irritation. At one time, sulfur dioxide was considered to be a major factor in the Los Angeles smog problem, but it is no longer so considered. (11)

Paradoxically, the Los Angeles smog occurs in its severest form on non-foggy days. Furthermore, only "smokeless" fuels such as natural gas and fuel oil are burned in the Los Angeles area, (5) so that smoke from this source is probably not a major factor. Hence, as applied to the Los Angeles condition, the designation smog is a misnomer.

Air Pollution from Combustion Processes

The most serious problem in air pollution is that which results from the combustion of fuels. This holds particularly true in Great Britain, where waste products of combustion are considered to be, by far, the major source of air pollution. In the United States, this is probably also true, although because of lower average population densities, generally more favorable meteorological and topographical conditions, and the employment of superior fuels as well as methods of fuel combustion (especially for domestic heating and railroad transportation), the problem is not nearly so acute as it is in Great Britain.

In the United States, some 600 million short tons of solid fuels and oil are consumed annually. (12) The corresponding consumption in Great Britain is approximately one-third that of the United States. (13) Oil accounts for roughly 25% of the U. S. fuel consumption and only 5% in Great Britain. Both in the United States and Great Britain, the generation of electrical power accounts for about 20% of the total fuel consumption and domestic heating for roughly another 20%. (12, 13)

For Great Britain, the estimated annual discharge into the atmosphere of pollutants from combustion processes is around two million tons of smoke, one million tons of fly ash, and five to six million tons of sulfur dioxide. (2, 13)[c] A rough estimate of how these pollutants are derived from various combustion operations is given in the Table I, prepared from data included in Ref. 13.

TABLE I
Per Cent of Total Pollutants Discharged

	Smoke	Fly Ash	Sulfur Dioxide
Domestic	45	13	17
Power stations	Small	37	19
Railways	15	13	8
All other industrial operations	40	37	56

Comparative figures for the United States are not readily available. However, it is speculated, on the basis of the availability of superior domestic fuels as well as domestic heating systems in the United States and generally more up-to-date industrial combustion equipment, that the overall emission of smoke and fly ash on a per capita basis is appreciably less than in Great Britain. Sulfur dioxide pollution on a per capita basis is probably comparable for both countries since American and British fuels are of comparable average sulfur content.

Smoke

Smoke has long been the obvious manifestation of air pollution from combustion processes. However, since smoke is indicative of inefficient utilization of fuel it is no longer tolerated by modern industrial operations (especially power plants) except possibly for brief periods during rapid load changes or abnormal operation. Unfortunately, high fuel economy is not equally important in the operation of many small industrial and most domestic installations, as a result of which these are probably the chief sources of smoke pollution today.

The logical remedy for smoke pollution is smoke prevention, which, in turn, is chiefly a matter of proper combustion. St. Louis and Pittsburgh are classic examples of formerly-polluted areas which were effectively cleaned up by the enforcement of smoke prevention measures. The enforcement of these measures also resulted in the abatement of sulfur dioxide pollution. The basic measures employed in these areas are: (1) fuel users who wish to burn high-volatile fuels must employ mechanical fuel-burning equipment, (2) fuel users who do not wish to use such equipment must use "smokeless" fuels, and (3) solid fuels containing high-sulfur refuse must be washed. (5)

Fly Ash

The emission of fly ash depends largely upon the type of fuel, the method of burning, and the type of dust collection equipment employed. With pulverized-coal firing, around 80% of the ash charged with the fuel is emitted from the furnace with the flue gases, chiefly as particles of fused ash, predominantly smaller than 325 mesh, with small amounts of combustible matter. Without adequate dust collection facilities, the combustion of coal in pulverized form is one of the chief sources of dust pollution of the atmosphere. (5)

With stoker firing, some 5 to 40% of the ash in the coal charged may leave the furnace with the flue gases, accompanied with combustible material in concentrations ranging from 10% to as high as 85% of the total weight of fly ash. More than half (by weight) of the fly ash will commonly be particles larger than 325 mesh (44μ) (5)

From the standpoint of minimizing fly ash emission, at least, cyclone furnace firing of crushed coal appears to be the preferable method for burning coal. [d] Only 10% or less of the ash in the coal charged leaves the furnace as fly ash containing small amounts of combustible matter. The remainder of the ash is withdrawn from the bottom of the furnace as molten slag. (5, 14)

Current ordinances on permissible fly ash emission from power plants range between 0.85 to 2.5 lb./1000lb. of gas adjusted to 12% CO_2 content. These figures are equivalent to 0.25 to 0.75 gr./cu. ft. of flue gas at 500° F., based on the gas containing 50% excess air. The present trend is toward the lower stack loading, which is the limit set by the so-called *A.S.M.E. Model Smoke Ordinance*. Therefore, it appears advisable for furnace and dust collector installations to be designed for stack loadings no greater than the lower figure. (5) This can be met without auxiliary dust collections equipment by the use of cyclone furnaces. (5)

The ash content of coal varies from as low as 1% (for certain washed coals) to greater than 20% (2) Assuming as a typical case the combustion of pulverized 12500 Btu. coal containing 10% ash, a stack loading of 0.85 lb. of fly ash/1000lb. of flue gas would correspond to a dust

[c] Another half-million tons of various dusts are estimated to be discharged from other industrial operation.(13)
[d] But see page 263.

collection efficiency of only 85%.[e] This is considerably lower than generally employed in modern power stations and central heating plants.[f] According to Johnstone,[5] 95% removal of fly ash from flue gases is insufficient to prevent air pollution. It is technically feasible to effect nearly 100% removal of dust from stack gases by the use of high-efficiency collector equipment such as electrical precipitators (usually in combination with mechanical collection equipment) and cyclone scrubbers.

As in the case of smoke pollution, industries other than the power industry contribute heavily to pollution of the atmosphere by dusts of various kinds. Domestic heating installations are probably of only minor importance from the standpoint of dust emission, because of the methods of burning and low flue gas velocities employed.

Sulfur Dioxide

The role of sulfur dioxide in atmospheric pollution[g] is a subject which has undergone much controversial discussion in the past and which is likely to undergo increased discussion and investigation in the future. The problem of sulfur dioxide pollution of the atmosphere appears unquestionably to be a real one. In most communities affected by air pollution, sulfur dioxide has been a significant contaminant, and, indeed, the concentration of sulfur dioxide is sometimes taken as an index of air pollution (cf. Fig. 1). Sulfur compounds probably first became recognized as serious atmospheric pollutants during the nineteenth century. At that time the tremendous increase in metallurgical and chemical operations contributed unprecedented concentrations of sulfur compounds to the atmosphere.

Sulfur dioxide in the air contributes extensively to the corrosion of buildings, metal objects, and fabrics. It is the principal cause of acidity in rain water and fogs. Concentrations of the order of 0.3 ppm. SO_2 or greater may be damaging to vegetation.[5] (Cf. Donora incident.) In its effect upon man, sulfur dioxide is intensely irritating to the eyes, throat, and upper respiratory system. Persons afflicted with asthma, bronchitis, and other chronic lung conditions or irritations of the upper respiratory tract are especially sensitive to sulfur dioxide in the atmosphere.[15] The permissible concentrations for man, for continuous eight-hour exposure, are currently set at about 10 ppm. for sulfur dioxide and 1 mg./m.[3] for sulfuric acid mist.[16] Sulfur dioxide and sulfuric acid are synergistic in their combined effects upon animal life, and there are indications that similar synergistic effects may exist between SO_2 and other atmospheric contaminants, so that concentrations of SO_2 considerably less than 10 ppm. may be detrimental to human health.[8, 16] The average person can detect about 3 ppm. of SO_2 by odor and 0.3 ppm. by taste.[3]

Sulfur dioxide oxidizes slowly in the presence of sunlight, yielding sulfur trioxide, which, in the presence of water vapor, is converted to sulfuric acid mist. When the humidity is high and natural fog exists, sulfur dioxide is absorbed by the droplets and is converted in solution to form sulfuric acid. Similarly, it is absorbed by wet surfaces, such as rain on a building. In this case, dissolved impurities may catalyze conversion of the dissolved gas to sulfuric acid. The corrosive action of sulfur dioxide is chiefly attributed to the formation of sulfuric acid.[2]

Recently[17] it has been suggested that the deleterious effect of atmospheric sulfur dioxide upon man and animals may result from its combination with metallic compounds (present in atmospheric dusts) as well as with ammonia (also present in the atmosphere) to form soluble sulfur salts, probably sulfites, which undergo auto-oxidation to sulfates. This is suggested as a logical explanation of how sulfur dioxide concentrations of only around 2 ppm., which is the highest concentration observed or estimated to have been present during the London and Donora disasters, could have been capable of causing serious irritation of the respiratory tracts. These small amounts of sulfur dioxide are believed to have been transformed into much larger quantities of soluble salts of an acidic character.

It has previously been observed that the removal of air-borne dust by means of an air filter or an electrostatic precipitator also reduced the sulfur dioxide content of the air.[18] This had been attributed to the adsorption of sulfur dioxide by the dust. More recently, however, it has ben calculated that the total capacity for chemical adsorption of sulfur dioxide on smog dust amounts to only about 2 ccm. of gas/g. of dust, and, under the worst smog conditions, this would not result in the transport of sulfur dioxide into the lungs of more than 0.1 to 0.2 cc. in 24 hrs.[17] Hence, the more recent theory of actual chemical combination of sulfur dioxide with metallic compounds in the dust seems a more logical explanation of this phenomena.

The combustion of fuels is the chief current source of air pollution by sulfur dioxide, although in the past, before economical methods for the removal and recovery of sulfur dioxide in waste process gases were put into practice, smelting operations, refineries, and chemical plants probably provided air pollution problems of a more acute nature. With stoker-firing, from 60 to 75% of the sulfur is converted to SO_2 and discharged with the stack gases. When pulverized coal is fired, and presumably when crushed coal is fired in cyclone furnaces, sulfur elimination with the stack gases amounts to 95% or more. With oil firing, sulfur elimination is virtually 100%. In coal-fired domestic heating installations, less sulfur is eliminated into the flue gases because of the lower combustion temperatures generally employed. Also, such installations generally burn a better grade of coal.[5]

Coal in the United States ranges in sulfur content from less than 0.5% to more than 4%. British coals encompass approximately the same range, and the average content for both American and British coals is about 1.5% sulfur. The average sulfur of American oils is also about 1.5%. Foreign oils tend to run higher, at around 4% sulfur.

Sulfur Dioxide as an Air Pollutant in Great Britain

The first serious concern of atmospheric pollution by sulfur dioxide in flue gases from power stations seems to have taken place in England in 1929, when a farmer won a suit against the Manchester Corporation for damages attributed to the Barton

[e] It must be kept in mind, however, that per cent collection efficiency, *per se*, is not a sufficient criterion, since particle size distribution as well as total rates of dust to be handled are important factors.

[f] For example, see page 263.

[g] References to atmospheric pollution by sulfur dioxide will imply simultaneous pollution by its accompanying oxidation products, sulfur trioxide and sulfuric acid mist.

Power Station. As a consequence of public pressure, catalyzed by the Barton case, the first large-scale flue gas washing process was added to the Battersea Power Station, which was then under construction in London. This was later followed by the installation of flue gas washing plants at the Tir John Station in Swansea, Wales, at the Fulham Station in London, and just recently at the Bankside Station in London. (2, 3, 9, 19-26)

The washing plants at Battersea and Bankside are essentially water-scrubbing processes, with the liquid effluent, after catalytic oxidation of the dissolved SO_2 to sulfate ion, being discharged into the Thames. The oxidation step is employed to avoid lowering the oxygen content of the river. The original Battersea gas washing plant operated for seven years prior to being shut down in 1940 because the plumes of condensed water vapor leaving the scrubber stacks were too obvious to enemy airmen. During this period, the scrubbing efficiency on flue gas from coal averaging 0.9% sulfur ran around 90 to 92%. At the end of the war, the original gas washing plant, after modification, was restored to service, and later a similar gas washing plant was added to the Battersea Power Station in order to take care of additional power generation facilities. The Bankside gas washing plant incorporates additional improvements over the current washing plants at the Battersea Station and currently removes sulfur dioxide from flue gases derived from fuel oil containing 3.8% sulfur with an efficiency of better than 95%.

The Tir John and Fulham installations employed the Howden-ICI non-effluent process. In this process, an aqueous slurry of chalk or lime is the basic scrubbing agent, but also large quantities of calcium sulfite and calcium sulfate crystals are recirculated in the slurry in order to prevent crystallization on the scrubber surfaces. This process eliminated the need for disposal of huge quantities of liquid effluent, but in its place, large quantities of spent mud containing the absorbed sulfur compounds had to be disposed of. The Tir John and Fulham installations were subject to severe operating difficulties (e.g., clogging of the scrubber). It appears that difficulties at the Tir John Station were so great that the washing plant soon had to be shut down, and its operation never resumed. The Fulham installation apparently operated more or less continuously until World War II, whereupon it was shut down along with the Battersea plant. In its original form, it operated several years on coal containing 0.9% sulfur with scrubbing efficiencies usually exceeding 98%. But in this form it was extremely troublesome and costly to maintain (the scrubber was subject to severe clogging difficulties). Later the scrubber design was modified to minimize the clogging problem, after which the scrubbing efficiency was reduced to around 90%. At the end of the war it was concluded that it would be too costly to put the Fulham washing plant back into use, and that its subsequent operation would be excessively expensive. Instead, a new process, the Fulham-Simon-Carves Process, which involves scrubbing with an ammonia liquor, processing ammonium sulfate and sulfur as by-products, is currently under development at the Fulham Station.

Nevertheless, according to Lessing, (27) the Howden-ICI process still merits further consideration. A scrubbing efficiency of 99.8% is currently claimed for the process, an "almost unchokeable form of highly efficient tower packing" is now available, (28) and the regeneration of the spent mud (largely calcium sulfate and sulfite) via ammonia and carbon dioxide from gasworks to produce ammonium sulfate and calcium carbonate (the latter to be recycled to the scrubbing plant) is indicated to be practicable. Other methods for recovering sulfur from the spent mud from the Howden-ICI process are discussed in Ref. 29.

Thus, in Great Britain, even before the London smog episodes of November 1948 and December 1952, the problem of atmospheric pollution by sulfur dioxide was already considered to be a critical one, and indeed, the problem appears to be particularly severe in the general vicinity extending within a few miles from the Battersea, Fulham, and Lots Road power stations in London. (8, 24)

Table I lists atmospheric concentrations of sulfur dioxide which have been reported for London and other British communities. Table II lists similar data for a number of American communities. These data are presented for purposes of rough comparison only, since, in general, data of this type have only a limited quantitative significance because of the impracticability of obtaining average samples over large areas, the extremely high variability in the concentrations diurnally and by season, as well as probable differences in the sampling and analytical techniques employed.

Currently in Great Britain, there are two opposing schools regarding the advisability and practicality of removing sulfur dioxide from power station flue gases by means of gas washing plants. (9) One school contends that the practical solution to the problem of objectionable emission of sulfur dioxide from power station flue gases is basically one of better dispersion of the gases into the atmosphere, and that this can be practicably accomplished by the use of tall stacks. Gas washing is opposed on the grounds that inefficient washing (e.g., less than 80 to 90% removal of the sulfur dioxide originally pres- and Pittsburgh) rather than a restricted measure involving only power station operators. Nevertheless, the last argument cited above is unfortunately all too reminiscent of the philosophy formerly practiced by some segments of industry, recently reviewed succinctly by H. B. duPont, Vice-President of the duPont Company, in an address, ***Management Looks at Air Pollution.*** (30)

> To quote Mr. duPont, *"There was a time, of course, when some manufacturers took a short-sighted view. If plant wastes killed fish in a river or fumes attacked vegetation round about, they were likely to weigh (with disregard of humanitarian, let alone aesthetic factors) the economic value of the fishing industry, or of the nearby gardens and orchards, against their own and argue that the jobs and the goods provided by the plant were of greater benefit. Therefore, they said, killing the fish or damaging the fruit didn't matter . . . but, (Mr. duPont concluded) times have changed, and the attitude of management has changed as well. Management now realizes that, quite aside from the social implications, pollution is bad business for industry itself.")*

The second school advocates the removal of sulfur dioxide from power plant stack gases, even in the face of the obvious deficiencies in the current gas washing processes, contending that emphasis on the dispersal rather than removal of a dangerous

TABLE II
Concentrations of Sulfur Dioxide in the Atmospheres of Various British Communities

	ppm. SO_2		
	Mean	Max.	Ref.
Lambeth, County Hall, London			
December 1951	0.22	....	8
1952 smog	.95	1.34	8
1948 smog	.51	0.75	8
Mean for Central London Sites			
1952 smog	.91	1.26	8
1948 smog	.46	0.67	8
Mean for Outer London Sites			
1952 smog	.35	0.56	8
1948 smog	.19	.31	8
Mean for all London Sites			
December1951	.12	....	8
1952 smog	.57	....	8
Seven British towns which reported fog on two or more days during the 1952 London smog			
December 1951	.13	....	8
1952 smog	.36	....	8
Eight British towns which reported no fog during the 1952 London smog			
December 1951	.05	....	8
1952 smog	.11	....	8
London — "Average Winter Density"	.18	....	2
Glasgow — "Average Winter Density"	.12	....	2
Leicester — "Average Winter Density"	.14	....	2
Leicestershire — "Average Winter Density"	.02	....	2
Leeds — Clear sunny day	.05	....	18
Cloudy	.14	....	18
Slight mist	.22	....	18
Fog (visibility 50 yds.)	1.96	....	18

pollutant is a short-sighted selfish approach. Although the use of tall stacks may reduce local pollution, this can be accomplished only with an increasing pollution of surrounding areas. (This seems to be an obviously important consideration in Great Britain, where there is a dearth of unpopulated areas between adjacent towns and cities). It has been estimated that about 20% of the sulfur dioxide emitted from a stack may be blown out to sea, but most of the remainder must eventually come to the ground, regardless of stack height, to corrode metals and buildings, to damage textiles, acidify the soil, etc. Finally, it is pointed out that during the London smog of December 1952, the height of the inversion was in the region of 600 to 1000 ft., which was not likely to have been capable of penetration by flue gases from even the tallest chimneys in London. (9)

The Beaver Committee on Air Pollution, which investigated the smog disaster of 1952, recently recommended that the equivalent of as much as 0.7 mil/kw. hr. be spent on gas washing until research produces less expensive methods. (13)

Sulfur Dioxide as an Air Pollutant in the United States

In the United States, the problem of sulfur dioxide pollution from flue gases appears to be a much less critical one than in Great Britain. This is attributed to generally more favorable meteorological and topographical conditions, lower average population densities, the much more extensive use of smokeless fuels such as oil and natural gas, and the use of generally more efficient methods of combustion, especially in the cases of domestic heating and small-scale industrial operations.

Table III summarizes data on atmospheric pollution by sulfur dioxide for a number of industrial as well as residential communities in the United States. To be noted especially is the marked reduction in sulfur dioxide pollution of the St. Louis atmosphere as the result of enforcement of the smoke abatement program. Similar results are claimed for Pittsburgh, although specific data do not seem to be available. In both St. Louis and Pittsburgh, the problem of smoke pollution is considered to have been entirely eliminated. For example, in Pittsburgh, the heating season total smoke was reduced by 85% and the heating season heavy smoke by 95% during the period 1945 to 1951. (21) The specific factors which most probably contributed to this reduction were the required use of low-volatile coal in hand-fired heating plants, washing of solid fuels to remove high sulfur refuse, changeover from coal to oil or gas, and dieselization of railroad locomotives. (5, 21) The only remaining atmospheric pollution problems in St. Louis and Pittsburgh are apparently relatively minor ones of fly ash and fumes. These, doubtlessly, are primarily of industrial origin. Hence, except for isolated instances, the problems should be solvable without great difficulty by use of relatively straightforward dust and fume collection methods.

An Approach to the Air Pollution Problem

Referring to Tables II and III, sulfur dioxide conditions in London and Leeds are noted to be of the same order of severity as in St. Louis and Pittsburgh before enforcement of smoke ordinances. In fact, the over-all problems of atmospheric pollution in London and Leeds appear basically similar to the former overall problems of atmospheric pollution in St. Louis and Pittsburgh, and indeed, probably represent as severe problems of atmospheric pollution as can be expected in the future for any other major industrial area in the United States or Great Britain (or almost anywhere else in the world, for that matter).

On this basis, therefore, it would appear that, except for unique cases such as the Los Angeles problem, the first step toward solution of any existing or future problem of atmospheric pollution due to combustion processes is the enactment of a smoke abatement program similar to the programs which proved so successful in St. Louis and Pittsburgh. A general program such as this has been recently proposed for all heavily populated areas in the United Kingdom by the Beaver Committee on Air Pollution. (13) For areas not subject to frequent temperature inversions and not too heavily populated, the use of tall or high velocity stacks to complement a smoke abatement program may be justified.

The Beaver Committee, cited above, has recommended a smoke abatement program aimed at reduc-

TABLE III

Concentrations of Sulfur Dioxide in the Atmospheres of Various American Communities

Community	Year	SO_2 Concentration ppm.[h] Av.	Max.	Ref.
Los Angeles	1949-50	....	0.60	46
Los Angeles	1951	0.05	0.3	32
St. Louis (cold months)	1937	.25 [i]	1.86 [i]	46
St. Louis (warm months)	1937	.13 [i]	0.76 [i]	46
St. Louis (cold months)	1950	.04 [i]	.51 [i]	46
St. Louis (warm months)	1950	.03 [i]	.24 [i]	46
St. Louis	April 1954	.06 [i]	.17 [i]	47
St. Louis	April 1954	.10	.43	47
Pittsburgh (industrial area)	1931-32	.30	2.5	46
Donora (during smog disaster)	1948	....	2. [j]	17
Donora	1949	.15	0.50	46
Chicago — railroad station	1937	.67	2.54	46
Chicago — manufacturing area	1937	.50	3.16	46
Chicago — commercial area	1937	.41	3.16	46
Chicago — residential area	1937	.16	0.47	46
Whiting, Indiana	June 1954	.17	1.22	47
Baltimore — industrial area	1950	.07	0.46	46
Baltimore — rural area	1950	.02	.11	46
Cincinnati — industrial and commercial	1947-51	.06	.46	46
Cincinnati — residential area	1947-51	.04	.3	46
Cincinnati — rural areas	1947-51	.04	.31	46
Cincinnati — all areas	1947-51	.06	.46	46
Cleveland (industrial area)	1949-50	.04	.49	46
Salt Lake City	1919-20	.04	....	46
Yonkers	1936-37	.03	.75	46
Charleston	1950-51	.02	.18	46
Charleston	November 1953	.11	.63	47
Washington, D. C.	October 1953	.09	.35	47
Philadelphia	October 1953	.09	.22	47
Akron, Ohio	Last Spring 1954	.09	.22	47
Elizabeth, N. J.	December 1953	.20	.38	47

h SO_2 equivalent to total sulfur content of atmosphere unless otherwise stated.
i SO_2 as such.
j Calculated estimate.

ing the total smoke in all populated areas by 80% in 10 to 15 yr. Government subsidization in the form of tax benefits, loans, and outright grants are advocated for the purpose of expediting the program. This Committee further concluded that the washing of flue gases was desirable provided that the process employed removes not less than 90% of the contained sulfur dioxide (under these conditions, objectionable pollution in the immediate vicinity of a stack because of cooling of the gases would be unlikely), and that the cost of gas washing was justified by the various advantages of a cleaner atmosphere, even if it amounted to the equivalent of 0.7 mil/kw.-hr. For some time now, all new power stations have been required to leave space for gas washing facilities, should such be required at some future date. [5] Immediate gas washing, however, has not been mandatory, except for the power stations previously cited.

The above British proposal, which requires the cooperation of domestic as well as industrial consumers of fuels, seems to be an excellent, realistic approach. Heretofore in Great Britain, industrial consumers, especially power stations, seem to have had to bear the brunt of the burden of pollution abatement, which seems unrealistic, inasmuch as the estimated annual cost of property damage alone (which discounts damage to crops and health) attributable to the emission of sulfur dioxide from domestic heating installations ($35,000,000) slightly exceeds that for power stations ($32,000,000). The corresponding estimated cost of damage due to smoke from domestic installations ($104,000,000) is about 75 times as great as that due to power stations ($1,400,000). [9,13] The total property damage due to atmospheric pollution in the United Kingdom has been estimated to run around $700,000,000 annually, roughly $14 per capita. [13, 22]

In the light of recent indications that sulfur dioxide and atmospheric dusts may be synergistic in their effects upon human and animal well-being, by virtue of combination of sulfur dioxide with components of the dust, ultimately to form soluble, acidic sulfates, it would seem especialy important in currently polluted areas, such as in Great Britain, where the domestic emission of sulfur dioxide cannot readily be reduced by the use of fuels of reduced sulfur content, to provide for a minimum emission of dusts and fumes from industrial installations.

From the standpoint of current publicity at least, the Detroit-Windsor area (currently the third largest industrial area in North America) seems to be the only major area in North America (other than Los Angeles) for which any major air pollution problem is indicated. In this area, some 16,000,000 tons annually of bituminous coal and other solid fuels containing an estimated average sulfur content of about 1.5% are consumed for domestic and industrial purposes, in addition to considerable quantities of fuel oil and natural gas. According to Katz, [31]

> "In the light of what is known of pollution in other industrial areas, peak concentrations as well as means values (of sulfur dioxide observed in the Detroit River area) indicate more serious sulfur dioxide conditions than in polluted areas such as Los Angeles, Yonkers, New York, some of the industrial regions in Great Britain, and even the Trail, British Columbia area [3] before full employment of remedial measures. The possibility of a major disaster in the Detroit River area is rendered unlikely only on the grounds of its topography, but with increasing industrialization, toxic levels of pollution are being built up to serious proportions. Smog visitations of several days' duration have (already) been noted during temperature inversion periods in the Detroit River area."

Steps are reportedly being taken to put into effect a St. Louis-Pittsburgh type of pollution abatement program to this area.

Table III shows unusually high means as well as maximum sulfur

dioxide concentrations for the industrial and commercial areas of Chicago in 1937, considerably higher even than for St. Louis and Pittsburgh before corrective measures were taken. Although current figures for Chicago proper are not available for comparison, current values reported for Whiting, Indiana indicate that at least some corrective measures have been taken to reduce air pollution in this general area. To be noted also in Table III are the considerable concentrations of sulfur dioxide currently reported for Elizabeth, New Jersey, which is located in what is probably the most highly-industrialized area in New Jersey.

In the case of the Los Angeles problem, smog was at one time directly attributed to sulfur dioxide pollution, the main sources of which were petroleum refineries. Correction of these sources of sulfur pollution, along with other corrective measures, resulted in a 50% reduction of sulfur dioxide emission for 1951 as compared to 1948, but the smog problem was not alleviated. [11, 32] The Los Angeles smog is currently attributed to air pollution by oxidation products of hydrocarbons, which in turn, are attributed mainly to the widespread practice of rubbish incineration and to exhaust gases from the unusually high number of automotive vehicles operated in the area. [33] Legislation reportedly is now going into effect to eliminate incineration as a source of pollution, and the problem of pollution by automotive exhaust gases is undergoing further investigation. [34]

Elimination and Removal of Sulfur Dioxide From Flue Gases

The removal of sulfur from fuels before use has been considered in the past and seems worthy of further consideration. A process has already been developed for the removal of sulfur from oil, but this is not yet economically attractive. [35] In the case of coal, much of the inorganic sulfur appears removable by efficient coal-washing methods, but removal of the majority of the sulfur content (*e.g.*, organic sulfur) without serious deterioration of the heating value has not yet been accomplished, regardless of economic considerations, and does not appear likely to be accomplished soon. [26, 36]

Fly Ash as an aid to Sulfur Dioxide Removal

As previously discussed, there are strong indications that reduction of atmospheric pollution is assisted by the efficient removal of atmospheric dusts — fly ash in the case of combustion processes. In this connection, it is of interest to note that the government buildings in the Washington, D. C. area are heated by means of steam generated in central stations, two in Washington proper, and a third in Virginia, which services the Pentagon Building. Stringent air pollution standards are presumably in force in Washington, D. C. proper, because of the prevalence of white limestone buildings in the city; yet these central heating plants, which employ underfed retort burners and only stub (high velocity) stacks, are able to operate on coal containing as much as 3% sulfur. The only indications of atmospheric pollution due to these heating plants have been minor complaints of sulfur dioxide odor only several times during each heating season (generally on still, foggy days), at a single location about two blocks from the West Plant in Georgetown. This is attributed to inability of present dust collection system to meet the current specifications of 98% removal of fly ash for this plant. Additional dust collection facilities to correct this deficiency are currently being installed. On the other hand, the Central Plant (in the heart of the city) operates on a specification of only 94% removal of fly ash, and, reportedly, has never been a cause of complaints due to air pollution. The Central and West Plants currently employ electrostatic precipitators only; mechanical dust collectors are being added to the West Plant. There are currently no specifications on fly ash removal for the Pentagon heating plant, evidently because the Pentagon Building is air-conditioned, is of concrete rather than limestone construction, and is located in an area much less densely populated than Washington, D. C. proper. This heating plant operates only on mechanical dust collectors; yet no complaints of atmospheric pollution are reported regarding its operation. [37]

Inasmuch as sulfur dioxide is indicated to combine with atmospheric dusts, so that removal of the latter from flue gases may result in the simultaneous removal of appreciable quantities of sulfur dioxide, it may be less desirable to restrict the formation and emission of fly ash from a furnace, such as by the use of cyclone burners, than to allow free emission of fly ash from a furnace, but removing it efficiently from the flue gases before allowing the latter to be discharged to the atmosphere.

Wet dust collectors (*e.g.*, cyclone scrubbers) are highly efficient for the removal of fly ash from flue gases. Nevertheless, they have not been widely used for this purpose, quite likely because the removal of fly ash alone can be carried out more economically by the methods currently in vogue. However, in the one known commercial installation of this type, where flue gases from fuel oils containing 3.5 to 4.0% sulfur are being processed, the scrubbed gases (with very little of the sulfur dioxide removed) [k] have caused no complaints, contrasted with numerous complaints about the "bite" of non-scrubbed gases from nearby power stations using the same fuel and electrostatic precipitators. It would appear, therefore, in this case at least, that scrubbing removed some component(s) of the unscrubbed flue gases (sulfur trioxide and/or sulfuric acid mist?) more efficiently than did the corresponding precipitators. [37a]

Sulfur Dioxide Removal by Gas Washing

There are many installations within the chemical and metallurgical industries for the removal of sulfur dioxide from waste gases by means of gas washing processes (*i.e.*, gas absorption), with subsequent recovery of the sulfur values. [3] In fact, it has been arbitrarily stated that for industrial operations resulting in sizeable quantities of waste gases containing 1% or more of sulfur dioxide, it pays to clean up the air and recover the sulfur. [3]

The quantities of sulfur potentially recoverable from flue gases are tremendous. For example, during World War II, more than 30 million tons/year of sulfur were emitted to the atmosphere in the United States from the combustion of coal and oil alone. This amounts to more than ten times the U. S. consumption of native sulfur during these years. Power stations account for roughly one-fifth of the total fuel consumption within the United States. Yet there

[k] In this type of application, recirculation of the scrubbing water is the normal procedure. Therefore, only that amount of sulfur dioxide which is soluble in the bleed-off water is removed—which is not very much.

are no commercial installations for the recovery of sulfur values from combustion waste gases. The basic reason for this is the low concentrations in which sulfur dioxide is generally present in flue gases. At the same time, with otherwise practicable solvents, the equilibrium partial pressure of SO_2 over the solvent is significant or else is operationally difficult to maintain at a sufficiently low level. Hence, in the scrubbing of flue gases, it becmes necessary to work with exceedingly small absorption driving forces (*i.e.*, exceedingly small differences between the partial pressure of SO_2 in the gas being scrubbed and above the scrubbing liquor). The water vapor content of the flue gases fixes the minimum practicable liquor temperatures that can be maintained within the scrubber (regardless of the inlet liquor temperature). This is the wet bulb temperature of the flue gas, which runs at around 120° to 140° F. (49 to 60° C.). This, in turn, limits the minimum equilibrium partial pressure of SO_2 that can be maintained over a solvent of given composition.

Most metallurgical waste gases which are commonly processed for sulfur recovery contain 5% or more of SO_2. The *residual* SO_2 gas concentration after processing such gases for the recovery of sulfur is usually of the order of 0.3% SO_2, which is approximately the *initial* SO_2 concentration in power station flue gases produced from high-sulfur fuels containing around 4% sulfur. The recovery of sulfur values from flue gases from fuels of low or only average sulfur content (containing around 1.5% or less of sulfur and producing flue gases containing of the order of 0.05 to 0.10% sulfur dioxide) is obviously still more difficult. This is the problem the British power stations have had to contend with and with which the average power station in the United States would probably have to contend with.

[l] According to Ref. 9 and 20, these figures would appear to apply to a washing plant handling flue gases from a 120,000 kw power station burning approximately 450,000 long tons/year of coal containing 1.5% sulfur.

[m] In making this conversion and the ones which follow, a maximum station efficiency of 8900 Btu/kw-hr was assumed (that for a modern high-efficiency station) and a minimum station efficiency of 12500 Btu/kw-hr (that for a station of average efficiency).[48]

Economics of Sulfur Dioxide Removal By Gas Washing

The removal (without recovery) of sulfur dioxide from flue gases by gas washing (*i.e.*, gas absorption) has been practiced on and off during the past twenty years at four British power stations, as previously discussed. Currently, however, only the Battersea and Bankside washing plants are in operation, both of which use the Battersea process. From the point of view of the public (if not from the point of view of the operators) this process has been successful, as a result of which the original installed capacity of 130,000 kw. by now has been increased to slightly more than 500,000 kw. [20] Widespread application of the process, however, is highly unlikely, because of the vast quantities of liquid effluent which must be disposed of, and there is no recovery of sulfur values. The present-day cost of operation of the Battersea process at a new power station (which presumably includes capital charges of the order of 8 to 10% per year) has been estimated to run around 1.00 to $1.40/long ton of coal burned. [9, 20] [l] This corresponds to around 0.3 to 0.6 mil/kw.-h., depending upon the efficiency of the power station. The costs of operation would also depend upon the capacity of the power station involved, although the available data are inadequate for this to be readily evaluated. For a modern power station with an annual coal-burning capacity of a million long tons of coal (assuming a load factor of 86%), the present-day plant investment would be roughly $4,500,000, or about $11 to $15/installed kw., again depending upon the efficiency of the power station. [38], [m] Any of the estimated costs given above, or which follow below, must be considered only as rough guides, since the cost data which have been reported are frequently incomplete, ambiguous, or inconsistent.

Unless a use can be developed for the large quantities of sludge produced by the Howden-ICI process, it appears unlikely that operation of the present installations at Fulham or Tir John will ever be resumed or new installations considered. The initial investment as well as costs of operation are high, and the process has been notorious for operating and maintenance difficulties. Recent estimates of the costs of operation of this process at a modern power station range from about 1.40 to $2.40/long ton of coal burned [9, 20] corresponding to around 0.5 to 1.1 mils/kw. hr., [l] depending upon the efficiency of the power station. Again the capacity of the station will be an important factor. The investment for a Howden-ICI plant to handle the flue gases from a power station burning a million long tons of coal/yr. (86% load factor) would be roughly $7,000,000 or about 17 to $24/installed kw. [38]

The gas washing process currently being considered by the British is the Fulham-Simon-Carves Process [20, 38, 39] in which flue gases are scrubbed with a concentrated solution of ammonium salts of sulfur. Ammonia (either liquid ammonia or preferably, for reasons of economy, concentrated gas-works ammoniacal liquor) is added to the scrubbing liquor at a rate corresponding to that of the absorption of oxides of sulfur. Batches of the saturated liquor are withdrawn periodically and heated in an autoclave with a small amount of sulfuric acid to produce mainly ammonium sulfate (for sale as a fertilizer) and a smaller proportion of elemental sulfur. On flue gases which, presumably, were derived from the combustion of coal containing 1.2% sulfur, some 99% of the sulfur dioxide was removed on a laboratory scale in a single stage scrubbing system designed for 1000 cu. ft./hr. of flue gases. On a pilot plant scale, about 95% removal of sulfur dioxide was effected in a two-stage scrubbing system designed for 25,000 cu. ft./hr. of flue gases (which is equivalent to a coal-burning capacity of roughly 100 lb./hr. According to the preliminary estimates of Craxford, *et al.*, [38] total operating and capital costs for a washing plant of this type to handle gases from the combustion of a million long tons/year of coal containing 1.2% sulfur (estimated load factor 85%) would run between $0.13 and $0.36/long ton of coal burned, or from 0.04 to 0.16 mil/kw.-hr., assuming the purchase of liquid ammonia and sale of ammonia sulfate at approximately current U. S. market prices, 88 and $43/short ton, respectively. With cheaper ammonia, such as obtainable from a gas works or coke-oven plant, the estimates of Craxford, *et al.* indicate the process to be potentially profitable. According to Ref. 20, however, it is premature to attempt to make a reasonably reliable estimate of the cost of a commercial Fulham-Simon-Carves

plant, and it is optimistic to hope that it will make a profit; however, the process is expected to be cheaper than any of the previously discussed processes. Rees' contention seems borne out, for example, by the fact that Craxford, *et al.* assumed annual maintenance charges of less than 1% of the plant investment. Using 5% of the plant investment as a more realistic preliminary estimate of the annual maintenance charges, the total operating and capital costs are increased to around 0.46 to $0.65/long ton of coal burned or 0.13 to 0.30 mil/kw-hr. The plant investment is estimated to run between 6,000,000 and $9,000,000, or around 14 to $30/installed kw., depending upon the power station efficiency.

On the basis of the cost figures cited above, the Battersea and the Fulham-Simons-Carves processes (as well as the Howden-ICI process, marginally) fall within the economic requirements proposed by the Beaver Committee for justifying installation of gas washing facilities at a power station for the abatement of air pollution in the United Kingdom. However, as previously suggested, for pollution problems within the United States, and probably within the United Kingdom as well, the much more effective type of pollution abatement program is believed to be one which drastically restricts the emission of smoke from domestic as well as industrial installations and furthermore restricts the emission of all other forms of particulate matter from industrial installations. If the emission of particulate matter to the atmosphere were thereby minimized, then on the basis of the most recent findings, [17] it appears likely that sulfur dioxide concentrations would be reduced simultaneously to levels well below the tolerance level currently set for the most sensitive forms of plant life, which, in turn, is well below the levels set for human beings and animals. Furthermore, the environment for synergistic effects would be eliminated. If such measures are taken, then within the United States, at least, it appears unlikely that elaborate methods of flue gas processing for sulfur removal will ever have to be practiced specifically for the abatement of air pollution, but only on the basis of economic incentive.. Moreover, except for the Battersea Process, all of the other gas-washing processes which have been proposed are relatively complicated chemical processes. This is a serious deterrent to the application of gas-washing processes by utility companies, which are reluctant "to get into the chemical business," and undoubtedly will continue to be one. The ultimate solution, where sulfur removal is required for whatever reason, may well be a sulfuric acid plant operated by a chemical company alongside the boiler plant, receiving and processing the strong solutions from the gas washing, and returning them weaker and ready for further washing.

For the recovery of sulfur from flue gases resulting from the combustion of relatively high-sulfur fuels, the Fulham-Simon-Carves process would be expected to become increasingly economical. From a strictly technical standpoint, either the Battersea or the Howden-ICI process would also be applicable for this purpose; indeed the Battersea process is reported to be currently in use at the Bankside Power Station on flue gasses from oil containing 3.8% sulfur. However, any process in which recovery of sulfur values is not a goal must necessarily become increasingly uneconomical with increase of sulfur content of the fuel employed.

A number of processes have been proposed for the economic recovery of sulfur from flue gases from high-sulfur fuels. Among these are the Zinc Oxide process proposed by Johnstone and Singh in 1940, [36] and several ammoniacal processes, similar at least in general principles, to the Fulham-Simon-Carves Process. [40-43] In most, if not all of the latter processes, a portion of the spent scrubbing liquor is treated with sulfuric acid and steam to produce ammonium sulfate and strong sulfur dioxide gas instead of sulfur as the second by-product. This is essentially the process which has been employed so successfully at the Trail smelter in British Columbia. [3] In the Zinc Oxide process, an aqueous sodium sulfite-sodium bisulfite solution is used for the basic absorption. Zinc oxide is used for regeneration of the absorbent. Sulfur is ultimately recovered as liquid (or presumably pure gaseous) sulfur dioxide.

Apart from work which may be still going on at the University of Illinois under Johnstone, the only current work on the removal of sulfur from flue gases being carried out in the United States seems to be that carried out by Bituminous Coal Research, Incorporated, a research organization associated with the National Coal Association of Washington, D. C., which represents the producers of bituminous coal in the United States. Work was completed about a year ago at this laboratory on the oxidation of SO_2 in flue gases by the use of ozone in order to product SO_3, which eventually combines with water vapor to produce H_2SO_4 mist. This in turn is collected in some sort of mist collector. [44] This process was concluded to be technically successful but unattractive commercially, because of the prohibitive cost of the ozone required. Bituminous Coal Research next began planning the study of a process of catalytic oxidation of the SO_2 in flue gas, which would employ a catalyst, which can be used at temperatures up to 700 to 800° F. In this process, also, the sulfur would ultimately be recovered as H_2SO_4 in a mist collector. [45]

Conclusions

Although evidently a critical problem in Great Britain, the problem of air pollution, while much publicized, need not become a major one in the United States (nor for that matter continue to be one in Great Britain), provided reasonable precautionary and remedial actions are taken.

Combustion processes constitute the major source of air pollution in the United States, as in Great Britain. Except for highly unusual areas, such as Los Angeles County, which is subject to a unique combination of topographical, meteorological, and operational factors, problems of air pollution from combustion processes should be solvable in a relatively straightforward manner by the application of measures such as those which proved so successful in the formerly critical areas of St. Louis and Pittsburgh. These measures are included in the following list along with several additional measures which have been or are currently being put into practice in the still-critical Los Angeles area.

(1). Prohibition or controlled usage of high volatile fuels by domestic as well as industrial consumers.

(2) Washing of solid fuels to remove high sulfur refuse (*e.g.*, pyrites).

(3) Promotion of more efficient combustion of fuels, which is considerably assisted by equipment-licensing requirements.

(4) Reduction of industrial emissions by control and collec-

tion methods or by redesign of processes.

(5) Dieselization of railroad locomotives.

(6) Control of smoke from diesel engines in locomotives and trucks.

(7) Change-over from high-sulfur coal to oil or gas as fuels.

(8) Elimination of burning at public dumps.

(9) Minimization of private incineration of refuse.

In the case of waste gases other than from combustion processes, economic solutions for the prevention and/or elimination of air pollution from these sources can almost always be effected, even without regard to humanitarian and aesthetic considerations.

With regard to problems of sulfur dioxide emission to the atmosphere, it is believed that such problems will tend to become alleviated automatically in the course of restricting the emission of smoke and dust, which is the main objective of programs such as outlined above. This was demonstrated to be a fact in St. Louis and Pittsburgh. In the light of the most recent experimental and theoretical understandings, the toxicity of below "normal" tolenrance level concentrations of sulfur dioxide is attributed to soluble sulfur salts which result from the chemical combination of sulfur dioxide with metallic compounds present in atmospheric dusts. These soluble salts are capable of irritating the respiratory tract to a much higher degree than could result from the same concentrations of sulfur dioxide in the absence of other pollutants. It would seem especially desirable and important to investigate thoroughly this possibility and to ascertain the extent to which sulfur dioxide can be eliminated by efficiently removing dust from the atmosphere. On the basis of the above theory, it becomes increasingly important to minimize the emission of industrial dusts, such as fly ash, especially in areas such as in Great Britain, where the emission of sulfur dioxide to the atmosphere cannot be reduced through the use of appreciable quantities of cheap, low-sulfur fuels, such as natural gas, in place of the fuels currently employed. Also, to enhance the removal of sulfur dioxide, it may prove to be less desirable to prevent the formation of fly ash through the use of combustion methods such as cyclone burners than to allow its unrestricted formation as a potential absorbing agent for sulfur dioxide, but to prevent its subsequent discharge into the atmosphere.

In view of the enormous quantities of sulfur potentially recoverable from combustion waste gases, it seems only logical that serious consideration be given to the utilization of these resources, quite independent of air pollution considerations. In the case of chemical and metallurgical gases (which, in general, are much richer in sulfur dioxide than flue gases), the economic recovery of sulfur has been clearly demonstrated and is widely practiced. For flue gases from the combustion of high-sulfur fuel (say, containing around 4% sulfur) a number of potentially economical sulfur recovery processes have been proposed and at least one of these has been thoroughly proved technically on a pilot plant scale.[36] In the case of fuels of average sulfur content (*e.g.*, 1.5% sulfur), several plants are currently in operation in Great Britain for the removal (without recovery) of sulfur dioxide from power station stack gases. These current operations are claimed to be economical, but only when the costs of operation are balanced against the estimated damage which the sulfur dioxide would have caused, had it been permitted to escape into the atmosphere. In the light of evidence which exists today, the removal, without recovery, of sulfur compounds from flue gases is an inadequate solution to a problem of air pollution which logically needs to be solved by a broad, comprehensive program such as practiced in St. Louis and Pittsburgh. It appears reasonably possible that improved methods will ultimately be developed which will make it economically attractive to treat flue gases from fuels of average sulfur content, independent of air pollution considerations.

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A Review of the Air Pollution Research Program of the Smoke and Fumes Committee of the American Petroleum Institute†

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Executive Secretary
Smoke and Fumes Committee of the API

The cooperative efforts of the oil industry during World War I led to the organization, in 1919, of the American Petroleum Institute. The problem of pollution was recognized almost immediately, and early efforts on pollution control were directed to the problems of pollution of navigable waters. The Division of Refining of the Institute was organized in 1930 and included a Committee on Disposal of Refinery Wastes. This committee recognized that air pollution would eventually become a major problem for the petroleum industry, but at that time few refineries were located in areas where pollution of the air was of great enough concern to require corrective measures.

Following World War II and the enormous growth in population and industry on the West Coast, public pressure to halt the *smog* that plagued Los Angeles mounted rapidly. The California legislature enacted a law authorizing the formation of county air pollution control districts. The oil industry was subject to mounting criticism as being the chief contributor to air pollution in the Los Angeles area. Various regulations were passed governing the emission of atmospheric pollutants, but none of these proved effective in eliminating the nuisance. Within the Western Oil and Gas Association, an organization was formed to investigate the nature and origin of air pollution in Southern California. This organization, still active, has contributed considerably to the basic knowledge of the air pollution problem in Los Angeles through sponsored research.

*Shell Oil Company
Wilmington, California
†Presented at the 51st Annual Meeting of the Air Pollution Control Association held at Philadelphia, Pa., May 25-29, 1958.

Formation of the Smoke and Fumes Committee

By 1951 it became apparent that the oil industry would continue to be blamed for the bulk of the air pollution, and it was also realized that the problem is not peculiar to the Los Angeles area but is of national importance. Although Los Angeles continues to get more than its share of the publicity, the same undesirable effects can and do occur in other parts of the country and the problem is of concern to the entire petroleum industry. At a meeting of the Division of Refining in November 1951, the Smoke and Fumes Committee was organized to set up a program to determine factually the causes and methods for control of objectionable atmospheric pollution resulting from the production, transportation, manufacture, and use of petroleum and its products. It was recognized that proper decisions with regard to the control of atmospheric pollutants could not be made without accurate, scientific information. It was also felt that, should legislation be regarded as necessary in some instances, fundamental knowledge based on reliable research rather than on theory or hypothesis should be available to government organizations to avert restrictive and uneconomic rulings of the type that had proved unnecessary in the past.

To carry out this program, research projects were established at qualified research centers where investigations were designed to determine the mechanisms leading to air pollution. A qualified scientist was selected from the oil industry to serve as a full-time Executive Secretary to administer the program. A group selected from top level research people was organized as a Technical Advisory Committee to guide the research program. Each research project was provided with a Project Advisory Committee composed of highly qualified industry scientists. These Project Advisory Committees maintain close contact with the research workers to offer suggestions to guide the project and to insure that results of the work are made available as promptly as possible.

The Smoke and Fumes Committee organization also includes a Publications Committee. Information resulting from research activities sponsored by the Smoke and Fumes Committee is distributed to other committees of

the API; to interested organizations in industry, research, and government; and to the public. Through the efforts of the Publications Committee, the dissemination of information has a prominent place in the Smoke and Fumes Committee program.

The Research Program

The Smoke and Fumes Committee has just completed its fifth year of sponsored research. The first project was established at the Stanford Research Institute on May 1, 1953. Research at SRI demonstrated that hydrocarbons and organic matter in the air react with oxides of nitrogen in sunlight to produce *smog* type air pollution characterized by its oxidizing ability. In connection with this work, methods were developed for the analysis of compounds suspected to be important in ozone-forming reactions. Included were methods to determine nitric oxide, nitrogen dioxide, aldehydes, ketones, and olefins present in the atmosphere. An infrared analyzer for hydrocarbons was completed and used to monitor hydrocarbon levels. The SRI project was completed in 1955, but sponsored research in air chemistry has been continued at the Franklin Institute using facilities which permit a more detailed study of atmospheric reactions.

The research at the Franklin Institute to determine the nature of chemical reactions in the air leading to air pollution is one of the most outstanding projects in the Smoke and Fumes Committee research program. The project was originally established to study reactions occurring in sunlight of oxides of nitrogen, ozone, and nitric acid vapor with hydrocarbons of the types present in gasoline. The objective was to determine the nature and relative amounts of the products formed. In order to work at the low concentrations occurring in the atmosphere, new analytical methods were required. Under Smoke and Fumes Committee sponsorship, the long-path infrared spectrometer (popularly known as "Silent Sam, the Smog Detective") was designed and built in Philadelphia, and the long-path infrared analytical techniques were developed. The device is a combination of a reaction vessel in which controlled amounts of pollutants in air can be irradiated by artificial sunlight and a highly sensitive measuring device by which the products of the reaction can be individually identified during the course of the reaction. Actually two of these devices are in use by the Franklin Institute — one at the laboratories in Philadelphia where their studies are concerned primarily with synthetic mixtures, and one in a mobile laboratory presently located in Pasadena, California, where both naturally occurring polluted atmospheres and synthetic mixtures are examined.

Researchers at the Franklin Institute have been able to show the relative influence of paraffins and olefins in the rate of smog-forming reactions. They have demonstrated the effect of varying concentration of nitrogen oxides in the reaction rates and on the products formed. They have discovered a new compound, or class of compounds, originally identified as "Compound X", which is formed as a result of reactions of hydrocarbons and oxides of nitrogen. Compound X has recently been further identified as peroxyacyl nitrite.

Work is in progress to synthesize and purify peroxyacyl nitrite to permit detailed study of the compound and its reaction products. Preliminary attempts to synthesize the compound from peracetic acid and silver nitrate and to purify it by gas chromatography have resulted in decomposition of the product in the purification step.

Future plans for the Franklin Institute project include studies of air chemistry in other areas of the Los Angeles Basin as well as continued research on synthetic mixtures to determine more of the nature of reactions leading to air pollution.

At the University of California at Riverside, the Smoke and Fumes Committee is supporting research on the effect of organic materials in the atmosphere on vegetation. Oxidant-type damage to plants is unique and is believed to be caused by oxidized organic materials. Although the damaging substance has not yet been identified, certain hydroxy hydroperoxides may be involved. Typical oxidant damage is produced with a mixture of ozone and certain olefins in air. The University of California at Riverside is conducting an extensive study of the products of the reactions of ozone and unsaturated hydrocarbons in an attempt to identify the products responsible for the damage.

As a part of this program, a plant exposure box was built in conjunction with the Franklin Institute long-path infrared cell at Pasadena and arranged so that the fumigants could be circulated through the cell and the box continuously using the long-path infrared cell to study the course of the reaction while exposing the plants. Reaction time and concentration of the fumigants have been found to be as important, or possibly more important, than olefin structure in determining formation of the phytotoxicant from ozone-olefin reactions.

In the realm of atmospheric pollutants other than hydrocarbons and oxides of nitrogen, sulfur compounds are probably the most frequently mentioned. Sulfuric acid aerosol has been suggested as one of the causes of reduced visibility accompanying air pollution. The Smoke and Fumes Committee sponsored a research project at the University of Illinois to study the rate of photochemical oxidation of sulfur dioxide in air. Results of this study proved that the gas phase oxidation of sulfur dioxide in naturally polluted atmospheres in natural sunlight is not significant in effectively reducing visibility. One hundred hours of intense noonday sunlight would be required to produce sufficient sulfuric acid aerosol to reduce the visibility in the Los Angeles atmosphere to one mile.

Liquid phase oxidation of sulfur dioxide in fog droplets nucleated with metallic salts has also been studied in the laboratory, but the conditions required to oxidize SO_2 to SO_3 in fog droplets are so specialized as to make the occurrence of this reaction highly improbable in naturally polluted atmospheres.

The ever increasing use of petroleum products and the concern over air pollution from burning hydrocarbons has given rise to many questions concerning the nature and extent of the contribution to air pollution from industrial and domestic burning devices. A project was placed at the Armour Research Foundation in 1953 to determine the quantity of hydrocarbon pollutants emitted to the atmosphere by furnaces burning petroleum products. A gas burner and an oil burner, considered typical of domestic units, were operated in a laboratory. Analysis of the gaseous effluents established that under even the most severe conditions of maladjustment, hydrocarbons were not present in gross amounts, and in normal burning conditions the flue gases from both oil and gas burners

contained no detectable quantities of hydrocarbon. To verify the laboratory results, a field survey of 74 installations, including both domestic and industrial burners, was conducted. Only eight installations showed hydrocarbons present in flue gas — all in amounts less than 100 ppm. From these results it must be concluded that industrial furnaces using heavy fuel oil and domestic units using furnace oil or gas do not release significant amounts of hydrocarbon contaminants to the atmosphere.

In the field of atmospheric analysis, the Smoke and Fumes Committee has also made, or is making, significant contributions. At the Kettering Laboratory of the University of Cincinnati, a project was established to conduct air analyses of a number of United States cities to determine the oxidant concentration during periods of air pollution for comparison with Los Angeles atmosphere. No abnormal ozone or oxidant contents, as noted in Los Angeles during *smog* attacks, were found in other cities, but in many instances the sulfur dioxide content of the air was much higher in other cities than in Los Angeles, indicating again that sulfur dioxide does not cause the visibility reduction associated with polluted air.

At the Truesdail Laboratories in Los Angeles, a recently placed project concerns the collection and analysis of gaseous carbon compounds in the atmosphere to determine the amount of carbon of fossil origin by analysis of carbon 14 in relation to the total carbon present. Samples of the atmosphere have been collected during periods of extreme air pollution and during periods of little or no pollution. The gaseous carbon fractions have been *fixed* as barium carbonate, and radiocarbon assay of the carbonate fractions is in progress in another laboratory. No results are available from this survey as yet, but the project is mentioned here to illustrate the type of work in which the Smoke and Fumes Committee is participating in an effort to provide a better understanding of air pollution problems.

Some of the sampling studies sponsored by the Smoke and Fumes Committee have pointed out that the micrometeorology of a sampling area can be extremely important in planning and conducting an air sampling program. The most recent research contract of the Smoke and Fumes Committee was awarded to the North American Weather Consultants at Santa Barbara, California, to study meteorological effects on atmospheric sampling. The project is designed to provide a handbook to assist engineers in the field in the planning, conducting, and interpreting results from gas tracer tests. The project is essentially a literature search based on recent experimental work with tracers and supplemented by the best available theory wherever necessary. North American Weather Consultants have assigned a research staff to the project, and it is expected the project will be completed this year.

New Tools for Research

In the development of new tools for air pollution research, the accomplishments of the Smoke and Fumes Committee are worthy of note. In addition to the long-path infrared cell and the associated techniques already described, the researches sponsored by the committee have produced: (1) A successful technique for tracing air pollution from a single source; (2) Gas chromatographic methods of analysis for the determination of the composition of exhaust gas; and (3) A method of detection of ozone suitable for use in continuous, portable instruments.

It is often desirable in the course of air pollution work to characterize quantitatively the pollution potential from a particular source. In a project sponsored at the Industrial Hygiene Foundation, a method was developed wherein the tracer substance, a small quantity of finely divided antimony oxide, is dispersed in a stack gas stream automatically for a desired period of time. Automatic sampling instruments, disposed at significant locations in the surrounding territory, are operated to collect the tracer material from the atmosphere. Analysis for the determination of the quantity of tracer in each sample involves neutron activation of the sample in a nuclear reactor and subsequent measurement of the induced radioactivity. This method provides the same high sensitivity normally associated with the use of a radioactive substance as a tracer, but avoids the hazards since the samples are made radioactive after the tests have been completed.

This tracer technique was successfully developed to determine the path of a gas from a given source. However, problems of the micrometeorology of the sampling area encountered in this project led to the placement of the North American Weather Consultants' project referred to earlier which will provide assistance in planning and interpreting these tests.

Through the Coordinating Research Council, the Smoke and Fumes Committee is contributing to the support of a project at the Bureau of Mines in Bartlesville, Oklahoma, on the development and application of gas chromatographic methods of analysis for the determination of the composition of exhaust gases. To date, the Bureau of Mines has developed equipment and techniques suitable for separation of the major portion of the hydrocarbon component of exhaust gas condensate into separate fractions with identification and quantitative measurement of each fraction. The technique developed to date is limited to C_9-and-lighter paraffins and C_8-and-lighter aromatics, olefins, and naphthenes, although some uncertainties exist in the identification of paraffins, naphthenes, and olefins above the C_6 molecular weight range. At present, methane is not collected by the sampling technique, but development of a method of analysis for methane by gas chromatography is in progress. In this project studies are currently under way to extend the analytical techniques to higher molecular weight materials through C_{10} and to oxygenated constituents of exhaust gas.

Since ozone formation is one of the principal indications of the extent of photochemical reactions in polluted air, a project was set up at the Armour Research Foundation to develop an instrument for continuous measurement of ozone in the atmosphere. A method of detection suitable for use in portable instruments was developed to determine ozone concentrations in the range found in polluted air. The principle of the method requires a catalyst upon which small concentrations of ozone are quantitatively decomposed. The rate of heat evolution, and consequently the catalyst temperature, is proportional to the ozone concentration. A patent assigned to the API has been applied for, and Mine Safety Appliances Company has been granted a non-exclusive license to use the method. Difficulties in circuit design and problems in the behavior of the catalyst at extremes of temperature and humidity have delayed final design of this instrument. The Smoke and Fumes Committee discontinued support of this project in 1956. but work has continued under U. S. Air Force sponsorship. Al-

though the principle of the method has been established, much work remains to design and develop a complete working system.

API-APF Cooperative Project

During the past two years, many organizations working on air pollution have placed considerable emphasis on the role of automobile exhaust in air pollution. Dr. W. L. Faith, in a paper presented at the Golden Jubilee Meeting of the Air Pollution Control Association in June 1957 [1], said,

> "No matter how you define it or which smog manifestation bothers you, you can find a relationship between smog and some constituent of auto exhaust — the aldehydes in exhaust stink; carbon monoxide is toxic and thus a health hazard; unburned gasoline and oxides of nitrogen can react under favorable conditions to produce eye irritation and to damage vegetation; and smoke from partially burned lube oil can easily restrict visibility and irritate the lungs in enclosed spaces."

In June 1957 the Smoke and Fumes Committee joined in a cooperative effort with the Air Pollution Foundation to study the effect of fuel composition on air pollution from automobile exhaust. This study, as well as the work of others, has shown that the problem of air pollution from automobile exhaust is extremely complicated. Many variables in addition to fuels need to be studied before any conclusions can be reached. The facilities at the Stanford Research Institute, designed to study eye irritation from irradiated auto exhaust and described in the Air Pollution Foundation Report No. 18 [2], have been teamed with the Franklin Institute mobile laboratory including the long-path infrared spectrometer located in South Pasadena to study this problem. Under the conditions investigated thus far, the exhausts from all fuels tested have shown similar air pollution manifestations.

Publications

Through its Publications Committee, the Smoke and Fumes Committee is making a continuing effort to publish the results of its sponsored research activities as rapidly as possible. Researchers are encouraged to appear on the platform at technical and scientific meetings and to publish their findings in the technical journals.

Since 1955 the Division of Refining of the American Petroleum Institute has held an annual technical session on air pollution in connection with its Midyear Meeting. Researchers from the various sponsored projects have appeared on the API platform to discuss their findings. In addition, Smoke and Fumes Committee sponsored research has been described at meetings of the American Chemical Society, at the Annual Meeting of the Air Pollution Control Association, and at the Annual Meeting of the Society of Automotive Engineers.

To date, the Smoke and Fumes Committee has spent approximately one and one-quarter million dollars to carry out this research program. The present rate of expenditure is about one-quarter million dollars per year.

Summary

In summary, may I again call to your attention the wide variety of research sponsored by the Smoke and Fumes Committee in the field of air pollution. The accomplishments of this committee include: (1) Research demonstrating that hydrocarbons and organic matter in the air react with oxides of nitrogen in sunlight to produce *smog* type air pollution characterized by its oxidizing ability; (2) Determination of the nature of many of the chemical reactions in the air leading to air pollution; (3) Studies of oxidant-type plant damage to determine the reactants and reaction products responsible for damage to vegetation from polluted air; (4) Experimental evidence that the oxidation of sulfur dioxide to sulfur trioxide in the atmosphere is too limited to produce significant reduction in visibility; (5) Tests to show that furnaces burning petroleum fuels do not release significant quantities of hydrocarbons to the atmosphere; (6) An analysis of the air in several United States cities showing absence of the abnormal ozone or oxidant content found in Los Angeles *smog*; (7) Analysis of the gaseous carbon compounds in the atmosphere to determine the source of atmospheric carbon; (8) Investigation of meteorological effects on atmospheric sampling to assist in planning and interpreting gas tracer tests.

In addition, the Smoke and Fumes Committee has been responsible for the development of outstanding new tools for air pollution research, including: (1) A successful technique to trace air pollution from a single source; (2) Gas chromatographic methods of analysis for the determination of the composition of exhaust gases; (3) A method of detection of ozone suitable for use in continuous, portable instruments; (4) The long-path infrared spectrometer and the associated techniques for use of the instrument.

Many problems remain unsolved, but the research program of the Smoke and Fumes Committee has contributed substantially to the basic knowledge of the sources, mechanisms, and methods of control of air pollution and has assisted materially in the development of new and better tools for the use of our scientists in the continuing effort to provide clean air for our nation.

(See Comments on following page.)

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COMMENTS

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The investigation of atmospheric pollution by stack gases in the Engineering Experiment Station of the University of Illinois is now in its thirtieth year. Many studies have been made of the reactions of combustion products in stacks and in the air, and of methods for removing the pollutants at the source. The results of all of the work are available to the public in bulletins of the Experiment Station and in papers in technical journals. In the co-operative research contract with the American Petroleum Institute it was found that the photochemical oxidation of SO_2 gas in air in intense sunlight was not fast enough to account for serious reduction in visibility. However, it was pointed out that different results might be obtained by oxidation in the liquid phase, such as in the droplets of a natural fog. Ellis (1931) found that the ratio of sulfuric acid to SO_2 in a London fog is higher than in fog-free air. A similar observation was made after a morning fog in an American city.

A Study Was Made

Accordingly, a study was made of the rate of oxidation of SO_2 absorbed from air by suspended drops containing manganese and iron sulfates, which are known to act as powerful catalysts for the oxidation reaction in solution. The results of the work indicated that the rate of formation of acid in a fog nucleated by particles of manganese sulfate in air containing 1 ppm. SO_2 might be as much as 500 times as fast as the photochemical oxidation in intense sunlight. This conclusion has been verified recently by measuring the rate of acid formation from dilute SO_2 — air mixtures containing fogs nucleated by very small particles of manganese and iron salts. The reaction proceeds in the dark and in light, and takes place when sodium chloride nuclei are also present, a condition that is apt to exist in the air of industrial cities even far inland from the sea coast.

The role of nuclei in other atmospheric reactions in air pollution is now being studied.

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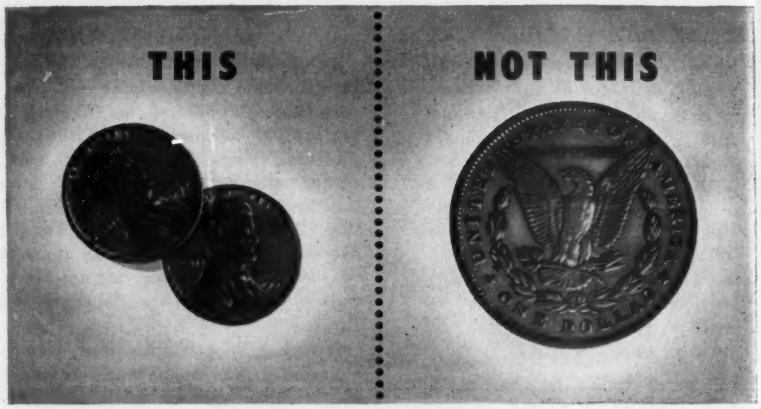

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Abstracts of Recent Legal Decisions Relating to Air Pollution

LEGAL COMMITTEE
Air Pollution Control Association

1. The People v. A & M Castings, Inc., 154 A.C.A. 543, 316 P.2d 779

(Appellate Department, Superior Court, Los Angeles, California, October 7, 1957)

Defendant was convicted of violating Section 24243 of the California Health and Safety Code which provides:

> "A person shall not discharge from any source whatsoever such quantities of air contaminants or other material which cause injury, detriment, nuisance or annoyance to any considerable number of persons or to the public or which endanger the comfort, repose, health or safety of any such persons or the public or which cause or have a natural tendency to cause injury or damage to business or property."

On appeal, defendant contended that the conduct prohibited by Section 24243 of the Health and Safety Code is defined in essence as a public nuisance by California Penal Code Section 370. By the provisions of California Code of Civil Procedure Section 731a, conditions arising from the operation of a plant in an area zoned for such operation shall not be deemed a public nuisance unless there is proof of unnecessary or injurious methods of operation. Since there was no such proof, argued the appellant, the conviction could not stand. Section 731a provides as follows:

> "Whenever any city, city and county, or county shall have established zones or districts under authority of law wherein certain manufacturing or commercial uses are expressly permitted, except in an action to abate a public nuisance brought in the name of the people of the State of California, no person or persons, firm or corporation shall be enjoined or restrained by the injunctive process from the reasonable and necessary operation in any such industrial or commercial zone of any use expressly permitted therein, nor shall such use be deemed a nuisance without evidence of the employment of unnecessary and injurious methods of operation. Nothing in this act shall be deemed to apply to the regulation and working hours of canneries, fertilizing plants, refineries and other similar establishments whose operation produce offensive odors."

Held: Conviction affirmed. The title of the act by which Section 731a was added to the Code of Civil Procedure reads: "An act . . . relating to the use of the injunction in industrial or commercial zones." Section 731a cannot be construed as giving a new definition of "public nuisance" because the title of the act does not cover the matter, and under the California Constitution an act is void as to any matter not expressed in its title. Furthermore, there was evidence at the trial that defendant's operations did "produce offensive odors" so that the limitation of Section 731a does not apply in this case.

***2. Neubauer vs. City of Cleveland* (145 N. E. 2nd 315)**

In a proceeding against the City of Cleveland to abate the nuisance of burning of combustible waste on the lake front, the City claimed that pending the construction of a new incinerator it was without facilities to dispose of such waste except through burning on the lake front dump, and that in such emergency no injunction against the practice should issue. The Court of Appeals (Ohio) held that the burning by the City of combustible waste on the lake front constituted a nuisance *per se*, was carried on in violation of State Law and the ordinances of the City of Cleveland, even though there had been no regulations promulgated to supplement the city's Air Pollution Control statute; other methods of disposing of combustible waste were available and could be made to work on the lake front dump, and therefore an alleged emergency did not exist and the City was not entitled to continue to burn combustible waste until the construction of a new incinerator.

***3. Columbia Southern Chemical Corp. v. Johnson* — Tex. Civ. App. —, 297 SW2d 373 (1956)**

Action: Appeal from judgment for plaintiffs in case tried without a jury.
Facts: Columbia had a chlorine-producing plant located at the north end of a parking lot. When properly operated, no damaging gases were released but if the workmen made mistakes a heavy chlorine-filled smoke was released. One night smoke was seen belching forth and the next day the chrome on plaintiffs' cars was damaged. Proof of negligence attempted by *res ipsa loquitur*.

Held: 1. There was sufficient evidence to support the verdict, there being no other chlorine producing plants for many miles.
2. Damage to chrome was proven and the measure of damages is the cost of the repairs required to bring the property to the condition it was in immediately prior to the accident.
3. There was no proof of damage to paint so the trial court was wrong in allowing same.

Summary of the case: Judgment awarded plaintiff for damages to automobile chrome from emissions of gases containing chlorine. Fault of defendant was proven under theory of *res ipsa loquitur*.

4. *Hindman et al. v. Texas Lime Co.*, _____ Tex. Civ. App., _____ 300 SW2d 112 (1956), Reversed in part in _____ Tex. _____, 305 SW2d 947 (1957)

Action: Suit for injunction and damages for operating a nuisance against lessor and lessee.

Facts: Limestone Products Co. owned a limestone plant which it leased to defendant in April, 1953. In 1955 the operation of the plant was greatly increased and altered. As a result quantities of lime dust were diffused into the atmosphere and settled on the adjoining land. Plaintiffs were twelve used car dealers located various distances from the plant. They alleged that they were put to great expense attempting to keep the lime dust from eating the paint off the cars, being forced to wax and wash much oftener than otherwise and suffering some damages in spite of their best efforts.

Pleadings: No specific cars were mentioned in the pleadings nor were the costs expended in protecting any specific car or cars mentioned. Each plaintiff alleged total costs.

Trial Court: The plaintiffs testified that certain cars diminished in value because of the action of the lime and preventive measures taken against it. The jury returned a verdict for the plaintiffs, against both defendants, and awarded damages based on this evidence. The trial judge entered judgment for the lessor, notwithstanding the jury's verdict.

SUPREME COURT OF TEXAS

(Reversing in part) held: 1. If lessee's method of operating a factory alone accounts for the damage, the owner is not liable even though he constructed the facilities now contributing to the nuisance. Lessor may

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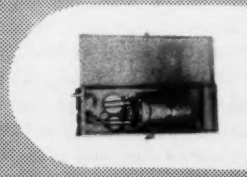

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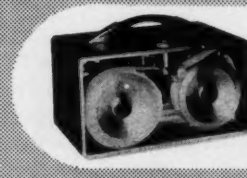

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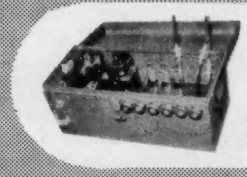

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be liable under some facts but not as a matter of law.

2. Damages were based on (a) extra expense occasioned by washing and waxing (b) decrease in the value of stocks of merchandise. It is not adequate proof of (b) to cite examples of diminished market value and ask the jury to infer what the entire damages were. Without an adequate evidentiary showing of some uniformity of damages, the "*sampling*" method is too uncertain a way to determine damages. 3. The misjoinder motion was made to apply to parties who had a common complaint, i.e., lime dust, and all sought injunction. Though the damages sought were different in each case it was within the discretion of the trial judge to refuse to sever the causes of action.

4. The fact that a date just within the statute of limitations was used as a beginning date for determination of damages, was not error. The jury would not necessarily conclude that all plaintiffs' damages would have commenced on that date.

There was a dissenting opinion.

Summary of the case: Several owners of limestone plants joined in single action by used car dealers whose cars were periodically covered by lime dust. Injunction refused on the grounds of public benefit derived from operation of the limestone companies, and suit returned to lower court for more proof on subject of damages.

5. *Riter v. Keokuk Electro-Metals Co.*, — Iowa — 82 NW 2d 151 (1957)

Action: Appeal from order granting injunction to abate a nuisance.

Facts: Defendant's plant was built in 1916 in an industrial valley. It was expanded several times and by 1942 had seven furnaces operating. The ferro-alloy produced contained 1.4% carbon, about half of which escaped in the smoke from the cupola. It settled on Plaintiffs' homes and property leaving black marks. Plaintiffs first complained in 1946. There was testimony several hundred thousand dollars had been spent in an effort to reduce the amount of escaping carbon and about 90% of what had escaped was, at the time of the suit, prevented from so doing.

Trial Court: Found present operation to be a continuing nuisance which, if not abated by a certain date, would cause an injunction to issue.

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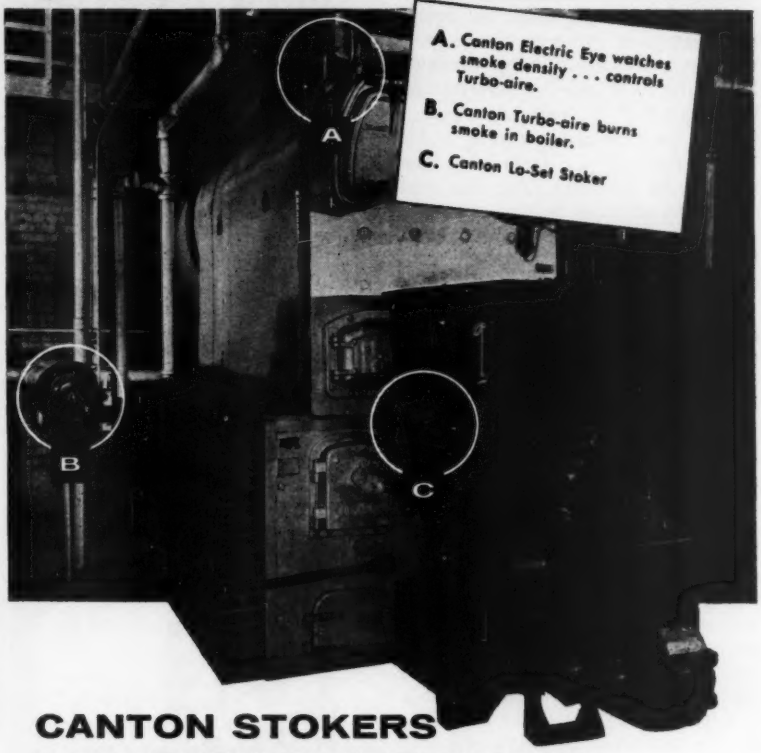
❷ CUTS COAL TONNAGE 17.5%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C

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Held: 1. Action not barred by statute of limitations and laches. Defendant's contention that plant was permanent nuisance incorrect because the nuisance was not the plant but the method of operation. Delay in bringing suit for nuisance will not necessarily establish laches or acquiescence such as will constitute an estoppel, but it may be a factor in determining the appropriate remedy.

2. The Iowa nuisance statute [Code 657.1, and 657.2 ICA] does not modify the common law rule that a private nuisance is the actionable interference with a person's interest in the private use and enjoyment of his land.

3. A person's right to pure air may be surrendered in part by his election to live in a city, particularly on an industrial locality which this part of Keokuk is.

4. Whether or not the operation of an industry is a nuisance depends on the reasonableness of conducting it in the manner, at the place, and under the circumstances in question.

5. The fact that the operation constitutes a nuisance does not mean it will be enjoined. Before an injunction will issue, the hardship to the Defendant and the community, if the injunction issues, must be balanced against the hardship to the Plaintiff if it is refused.

6. Here the health of the citizens was not endangered and the hardship on the Plaintiff was relatively small compared to what defendants would suffer by having to shut down the plant. Plaintiff's long delay in bringing action lends support to the belief that the condition isn't as serious as some of the testimony would indicate.

7. It is error to hold that where a nuisance is shown, the enjoined person is entitled as a matter of right to its abatement by injunction without reference to comparative benefits or injuries.

Reversed and remanded with leave to amend petition to claim damages.

Summary of the case: Action by plaintiff to enjoin operation of furnaces and cupola because of damage to plaintiffs' homes and property. Defendant showed that several hundred thousands dollars were spent on control measures and had substantially reduced emissions since initial complaint in 1946. The Supreme Court held the operation not nuisance *per se*. If the injunction to be issued, must be fully substantiated by the facts and showing of undue hardship

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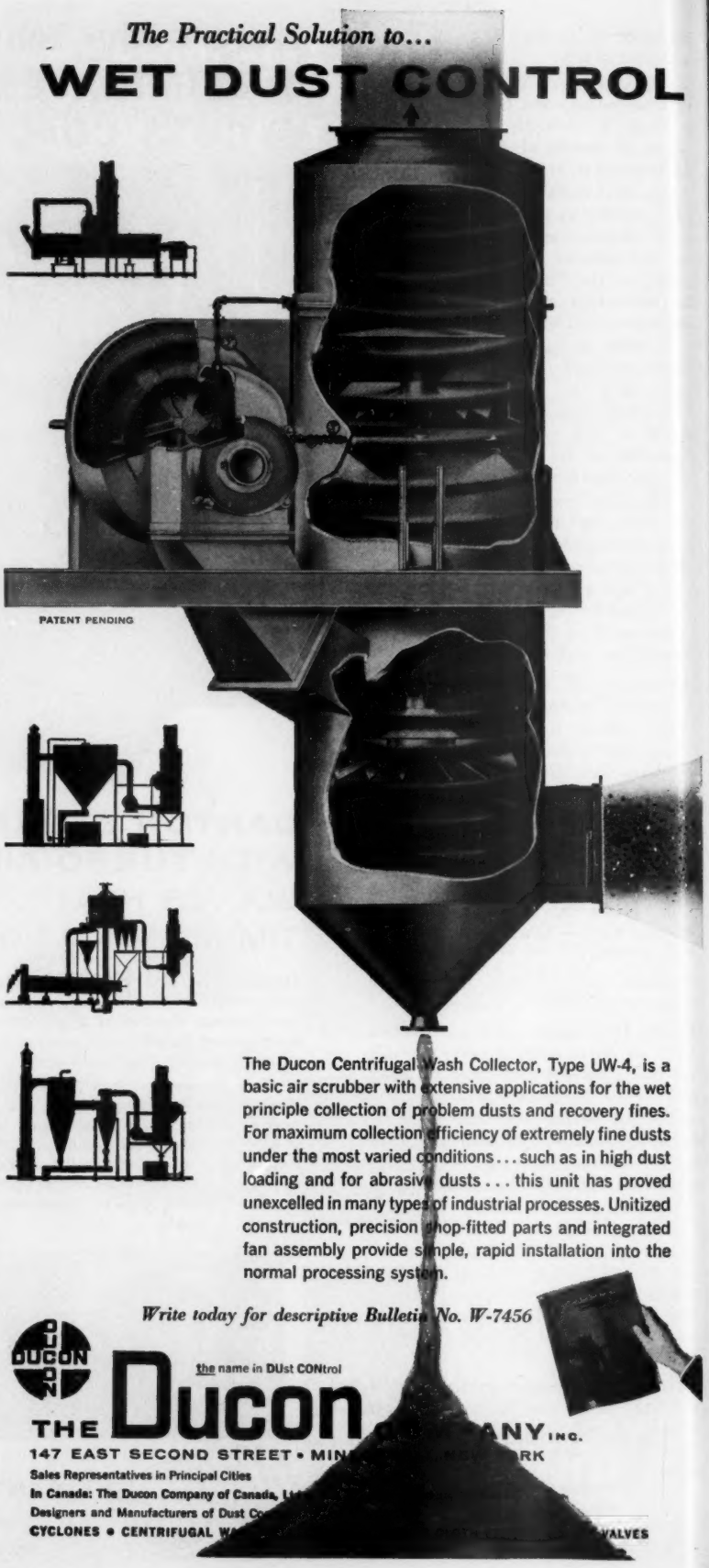

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upon plaintiff. The court questioned whether health was in danger and whether injunction necessary. The case remanded to lower court.

6. *Flippin et al. v. McCabe*, ——— Ark. ———, 308 SW2d 824 (*1958*)

Action: Appeal by plaintiffs from grant of only a partial injunction.

Facts: Defendants operated a battery of four charcoal kilns near a town, which kilns emitted smoke and volatile vapors into the air. After operating about a month plaintiffs sued to enjoin this operation. The trial court found that the smoke from the kilns settled close to the ground when the air was moist so enjoined operation of the kilns from December 15 to March 15. There was conflicting testimony as to the undesirableness of the smoke during other times of the year and the trial court ruled that no more than two kilns could be operated at once the rest of the year. Plaintiffs appeal from a refusal to enjoin the operation completely.

Held: 1. Though whatever materially and substantially impairs the enjoyment of one's homestead is enjoinable, not every nuisance is subject to injunction. This plant is not a nuisance *per se* and only such part of the operations that creates the nuisance should be enjoined.

2. The burden is on the complaining party to show nuisance in fact, in such a case, by clear and substantial evidence. Because of the highly conflicting testimony, are unable to say findings were against the preponderance of the evidence.

3. Introduction of testimony regarding effect of similar kilns in the area, not error. Because the kilns in question were in operation for so short a time, the experience of other persons near similar operations may have been of probative value.

Summary of the case: Operation of charcoal kilns not nuisance *per se* and court refuses to issue permanent injunction against operation of all kilns.

Wanted: Classified

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NITRIC OXIDE CONCENTRATIONS

(continued from page 239)

Park, Calif., has been carried out during the winter months of 1956-57. Concentrations up to 55 pphm. NO and 15 ppm. NO_2 have been recorded. The diurnal curves are bimodal. One maximum for NO occurred in the morning about 8 a.m., the other in the early evening. The concentration generally remained high between 5 p.m. and midnight, and several maxima and minima often occurred during this period. The NO_2 showed one maxima between 9 and 12 a.m. and another in the early evening. Minima for both gases occurred at about 3-4 p.m. and 4-5 a.m.

TABLE VII
Comparison of Nitric Oxide Concentrations on Clear and Cloudy Days

	NO Concentration Clear Days Cloudy Days 8-9 a.m. Period		NO Concentration Clear Days Cloudy Days 6-12 p.m. Period	
Month	pphm.	pphm.	pphm.	pphm.
December	20	8	13	9
January	23	12	14	7
February	23	6	8	5

Recordings occurred only with low wind velocities. In calm weather wind direction had no effect; with slow wind movement, 2-5 mph., recordings occurred only with directions along the axis of the "built-up" area. Concentrations were higher in clear than in cloudy weather. Diurnal and monthly average recordings followed closely the corresponding values of natural gas consumption in the area, suggesting that space heating is an important source of the nitrogen oxides in the winter. The contribution of traffic was approximately equal to the contribution of space heating but probably due to the concentration of the former along two major highways, its pattern did not resemble so closely the pattern of nitrogen oxides.

Acknowledgment

Mr. C. P. Smith of Pacific Gas and Eletric Company kindly made available the monthly and diurnal gas consumption records in Menlo Park, Palo Alto, and Northern California, on which Tables II and III and Fig. 5 and 6 are based. Our appreciation is expressed to Mr. Smith for this material. Our thanks are due also to Mr. G. E. Dillon of the California Division of Highways, San Francisco, for diurnal traffic data in Table I.

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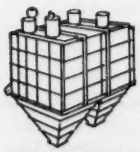

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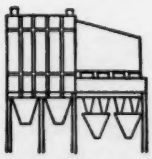

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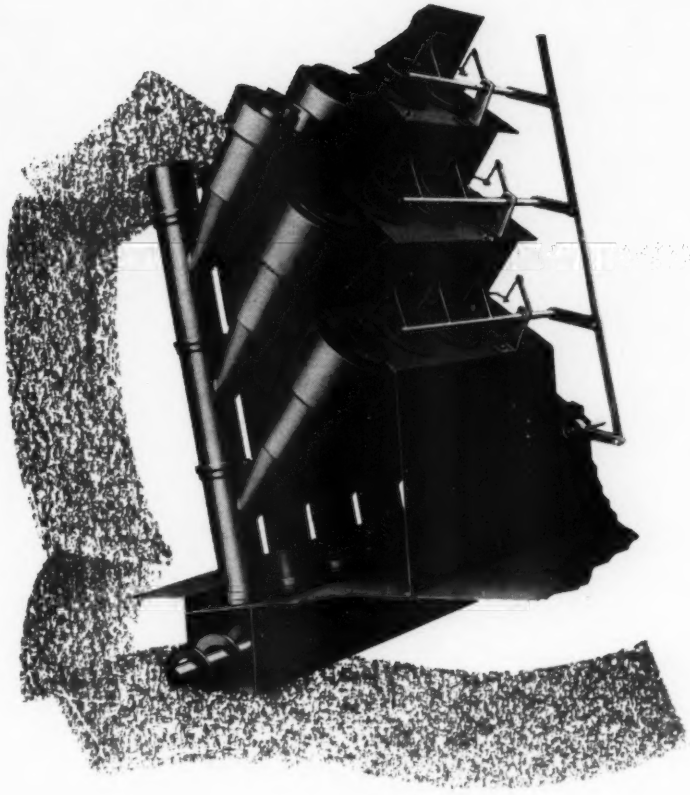

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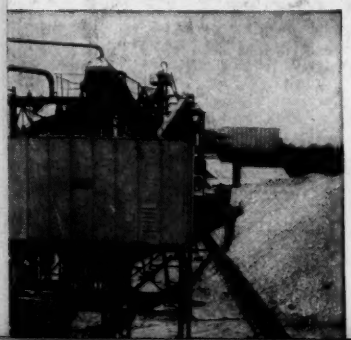

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